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POTENTIAL CHEMICAL SYSTEMS FOR INTRAMOLECULAR CYCLOADDITION CURES

POLYMER BRANCH
NONMETALLIC MATERIALS DIVISION

May 1979

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Final Report For Period September 1977 to September 1978

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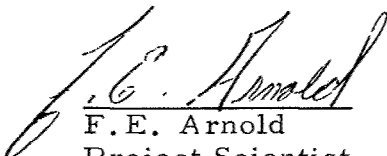WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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Literature Review

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

This report is concerned with an in-depth review of the chemical literature from 1957 to 1978 on intramolecular cycloaddition reactions. Selective hydrocarbon and heterohydrocarbon systems were synthesized and evaluated to demonstrate potential for inclusion into IMC curing matrix resins.

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic
Materials Division. The work was initiated under Project No. 2419, "Non-
metallic and Composite Materials," Task No. 241904, Work Unit Directive
24190415, "Structural Resins." It was administered under the direction of
Air Force Materials Laboratory, Air Force Wright Aeronautical Laboratories,
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Dr. F.E. Arnold as the AFML Project Scientist. Co-authors were
Dr. K.S.Y. Lau (Visiting Scientist) and Dr. F.E. Arnold, Air Force Mate-
rials Laboratory, (AFML/MBP).

This report covers research conducted from September 1977 to
September 1978.

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SECTION I. INTRODUCTION

The state-of-the-art method of fabricating fiber reinforced composites requires nonmetallic materials that exhibit low Tg and extensive flow to facilitate fiber wetting. The low Tg material is then transformed into the high Tg glassy state by a facile thermal induced addition reaction which excludes void producing volatiles. The mechanism by which the transformation to the high Tg glassy state, or curing, takes place will be directly dependent on the ultimate performance of the composite.

Current state-of-the-art matrix resins cure via intermolecular addition reactions that is very mobile linear or branched molecules vitrify by reactions occurring between chains. This method of cure requires extensive flow and is very dependent upon molecular mobility to reach completion. When molecular movement ceases unreacted cross-linking sites become "frozen" and curing stops. Raising the curing temperature will increase molecular movement, and more reactive sites are thus "unfrozen" allowing the curing process to continue. However, what this means is that the ultimate use temperature of the resin may only be as high as the curing temperature. Further, the resulting three-dimensional network formed tends to be brittle, limiting durability and performance.

Previous work (Reference 1) in our laboratory demonstrated a new curing concept for matrix resins which obviates all of the drawbacks inherent in the state-of-the-art intermolecular cure. The concept is an intramolecular cycloaddition or IMC cure. This consists of starting with linear mobile polymer chains which display flow and moldability at relatively low temperatures. The molecular mobility is subsequently arrested by having pairs of pendant groups along the polymer chain undergo an intramolecular cycloaddition reaction to form a more rigid higher Tg polymer structure.

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The IMC type of cure depends upon only a rotational movement of the polymer backbone which requires substantially less molecular mobility than the translational movement needed for the intermolecular cure. Therefore, the curing reaction can continue to completion long after the resin is in a vitrified state, and the resultant use temperature should be substantially higher than the cure temperature. Furthermore, because it is an intra-molecular reaction, a linear polymer is obtained which avoids the brittleness of a three-dimensional network structure.

The intramolecular cycloaddition reaction employed to demonstrate the proposed new cure concept was the thermal conversion of 2,2'-di(phenyl-ethynyl) biphenyl (1) to form 9-phenyl-dibenz[a,c]-anthracene(2) (References 2,3). The reaction is intramolecular and therefore independent of translational molecular mobility; it is volatile-free and gives an end product which is a fused aromatic structure.

(1)   (2)
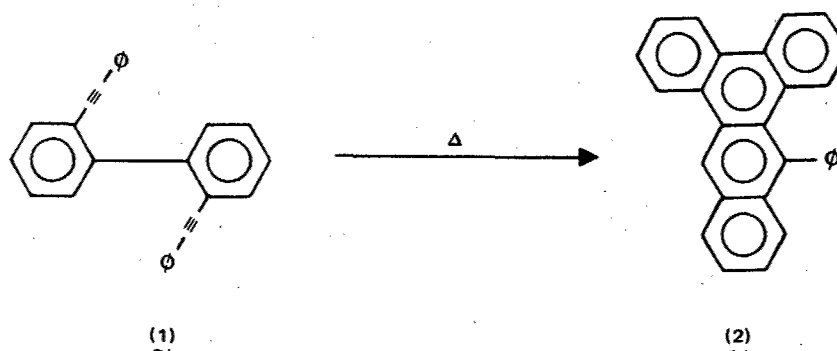
Two aromatic heterocyclic polymer systems were constructed to incorporate the acetylenic biphenyl moiety along the polymer backbone. Studies on the pre-polymer polyphenoxyphenylquinoxaline (3) showed that a $120^\circ C$ advancement in Tg could be obtained in the cured polymer (4) after an overnight cure at 245° (which corresponds to the exothermic maximum on DTA) (References 4,5).

(3) (Tg = 215°C)   **(4) (Tg = 365°C)**

The biphenyl intramolecular cyclization (IMC) site has also been con-
structed on an aromatic polyimide system (References 6, 7 and 8). The pre-
polymer 5 containing the hexafluoropropane group gave the lowest Tg.
Thermal curing studies of 5 again showed a substantial enhancement in Tg
with the formation of the cured polymer 6.

(5) (Tg = 185°C, TMA)

(6) (Tg = 310°, TMA)
(Tg = 325°, DSC)

This report consists of a review of the open literature concerning
cycloaddition reactions. It was our intention to synthesize and evaluate
selective hydrocarbon and heterohydrocarbon systems to demonstrate poten-
tial for inclusion into IMC curing resins.

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SECTION II. RESULTS AND DISCUSSION

A. LITERATURE REVIEW

In an effort to evaluate the extent of research in the area of thermally induced intramolecular cyclization of acetylenic compounds, an in-depth research of the chemical literature from 1957 to 1978 was conducted (Reference 9). The following is a summary of pertinent literature, emphasizing on thermal intramolecular cyclization reactions that produce new aromatic and heteroaromatic nuclei without evolution of volatile by-products.

The classical method of condensation provides entry to a multitude of aromatic and heteroaromatic structures. Small molecules are split off during the process which is usually catalyzed by an acid or a base (References 9b and c).
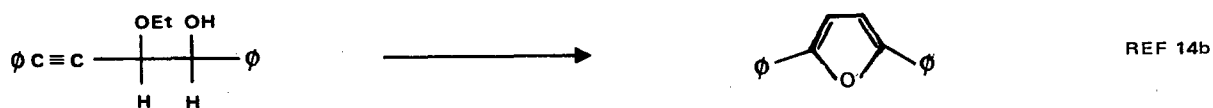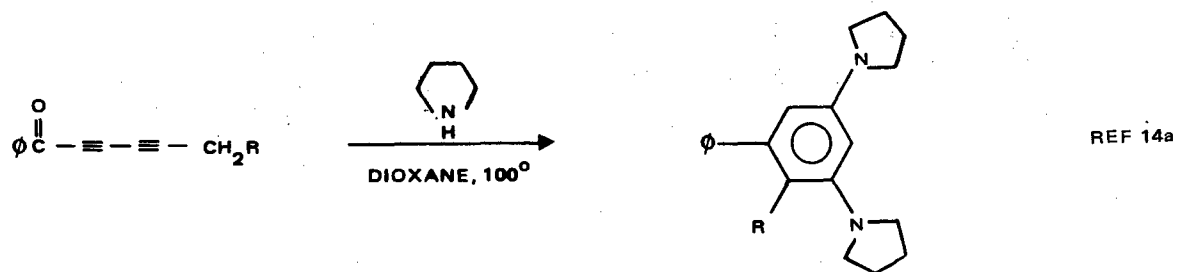
The generation of a conventional reactive intermediate on an aromatic ring for attack on another is an important method for linking aryl-carbon atoms. Ample examples are found in benzyne (Reference 10) and heteryne (Reference 11) chemistry. An account concerning the use of benzynes intramolecular reactions that lead to condensed polynuclear compounds has appeared recently (Reference 10).
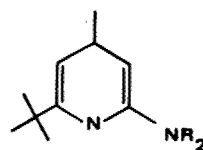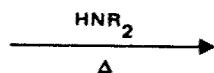
The symmetry-allowed electrocyclic photochemical ring closure of stilbene to dihydrophenanthrene is well known (Reference 12). The presence of an oxidant, e.g., oxygen or iodine, during the reaction causes facile dehydrogenation to give the fully aromatic phenanthrene. Application of this photocyclization-oxidation method has led to the formation of condensed polynuclear systems, e.g., phenanthridines (Reference 13a), chrysenes (References 13b and c) and phenanthrenes (Reference 13d).

$\dfrac{h\nu}{O_2}$

R_1 R_2 = H, CH$_3$

$\dfrac{h\nu}{C_6H_6, I_2}$

10-14%

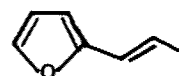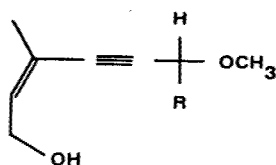$-CO_2Et$ $\dfrac{h\nu, I_2}{EtOH}$ $N-CO_2Et$
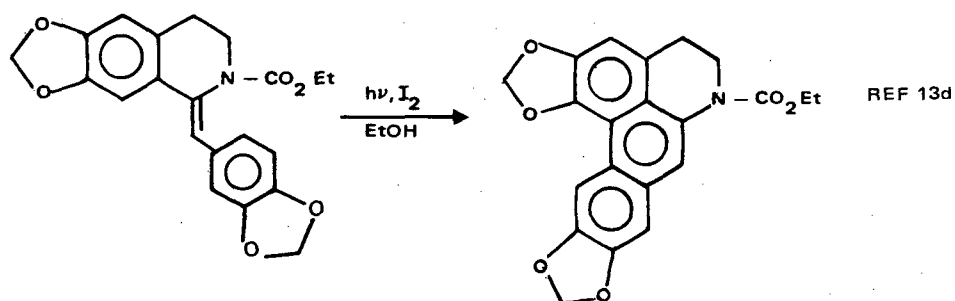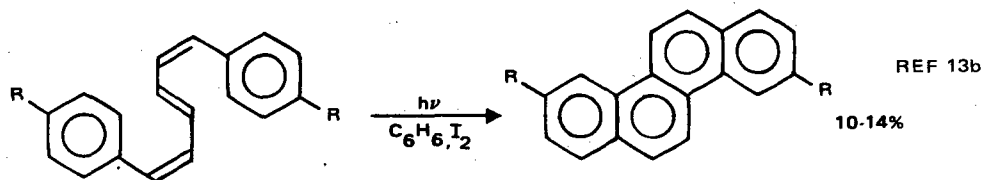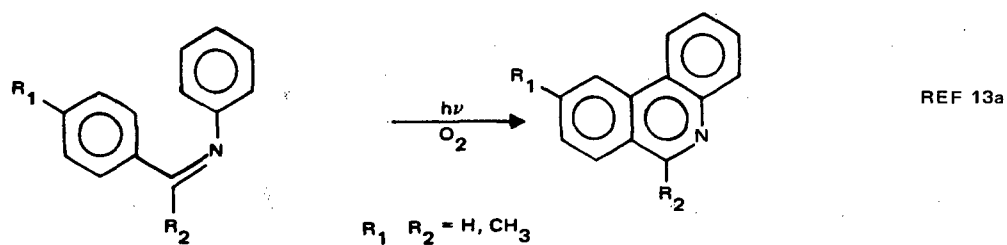
Conjugated and non-conjugated polyene-yne systems have been studied for their propensity in undergoing cyclization reactions under various conditions.

Organic bases (Reference 14) are capable of catalyzing the formation of heterocycles and benzenes from acetylenic compounds.
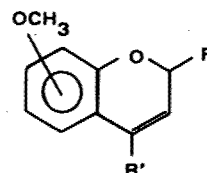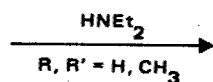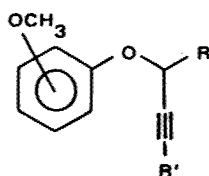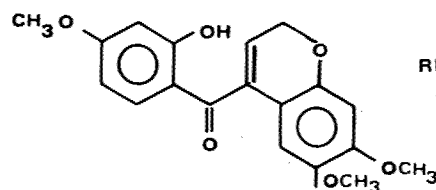
$\phi\overset{O}{\overset{\|}{C}} - \equiv - \equiv - CH_2R$ $\xrightarrow[\text{DIOXANE, 100}^\circ]{}$

$\phi C \equiv C -\overset{OEt}{\underset{H}{|}}-\overset{OH}{\underset{H}{|}}- \phi$ $\longrightarrow$

HNR$_2$ / Δ

REF 14c

tBuOK / DMSO

H OCH$_3$ R OH

REF 14d

OCH$_3$ R R'

HNEt$_2$ / R, R' = H, CH$_3$

OCH$_3$ O R R'

REF 14e

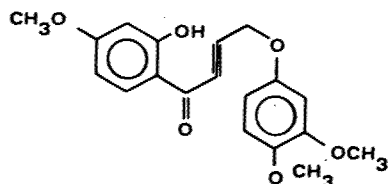CH$_3$O OH OCH$_3$ O CH$_3$

ϕNEt$_2$ / 180-185°

CH$_3$O OH O O OCH$_3$ OCH$_3$
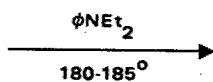
REF 14f

Compounds containing propargylic end groups are reactive towards bases by virtue of the facile isomerization of the propargyl group to the allenic structure. In weakly basic medium, the quaternary ammonium salts 7 and 9 undergo intramolecular cyclization to give aromatic structures 8 and 10 (Reference 15).

R R$_1$ N$^{\oplus}$ CH$_3$ X$^{\ominus}$ (7)

CH$_3$ N$^{\oplus}$ R$_1$ R X$^{\ominus}$ (8)

REF 15a

REF 15a, b, c

(9)　　　　　　　　　　　　　　　　(10)
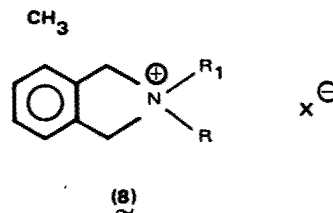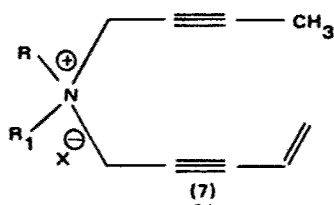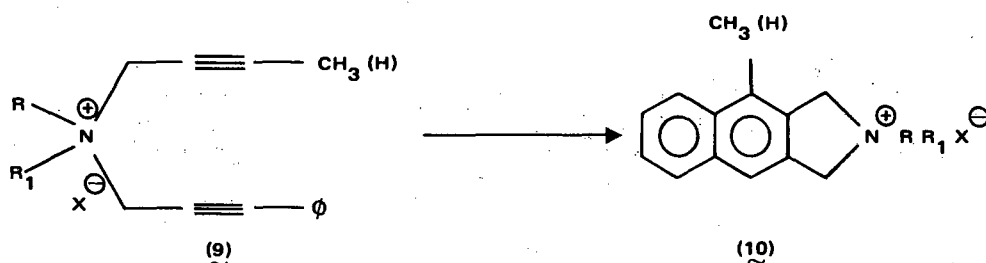
In the formation of 8 and 10, the propargylic-allenic rearrangement is a probable first step. The same mechanism seems operative in the transformation of 11 and 13. Although it has been suggested that cyclization takes place with the allenic-propargylic intermediate in the case of 11 (Reference 16a) and both the allenic-propargylic and the bisallenic intermediates intervene in the case of 13 (References 16b and c), the conclusions are by no means unambiguous. A bisallenic intermediate can be solely responsible for the


(11)　　(X = CH$_2$, O, S, NMe)　　　　　　　　　　(12)　　REF 16

(13)　　　　　　　　　　　　　　　　　　　　　　REF 16

7

(14)   (15)
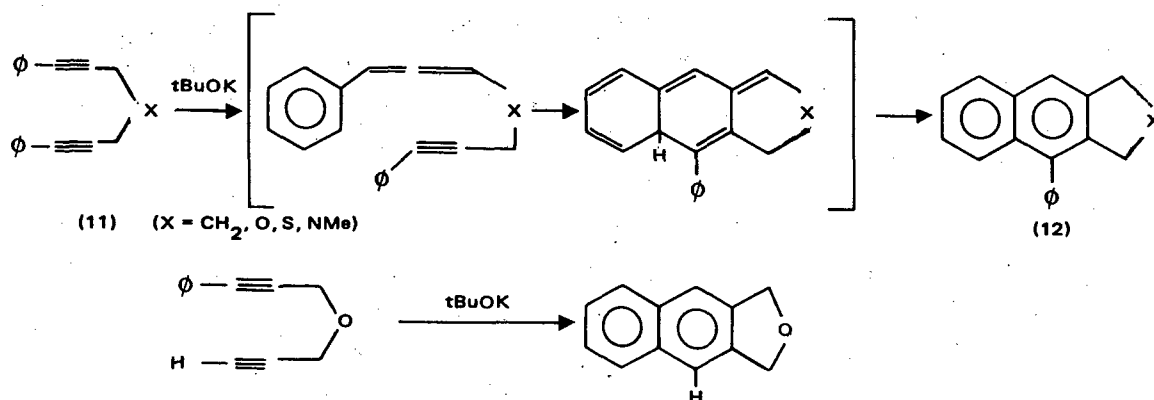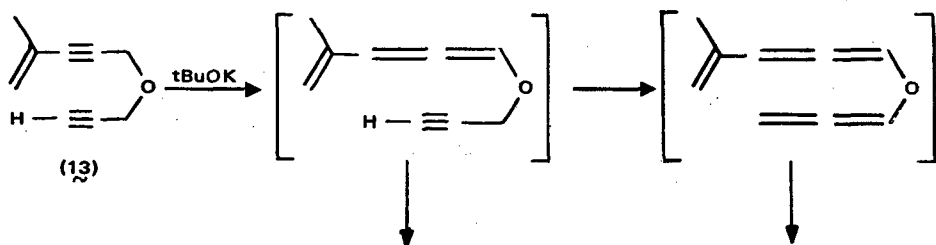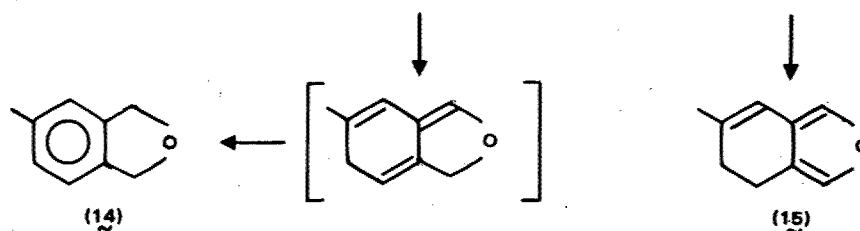
formation of 12, 14 and 15. In fact, in the latter case, 14 can probably arise from a facile base-catalyzed aromatization of 15. Further investigations (Reference 17) have shown that the naphthalene systems 12 are not the primary reaction products of the transformation of 11. The isolation of 16 supports the bisallene mechanism.

(11)   X = O, S, NCH₃

(12)   (16)
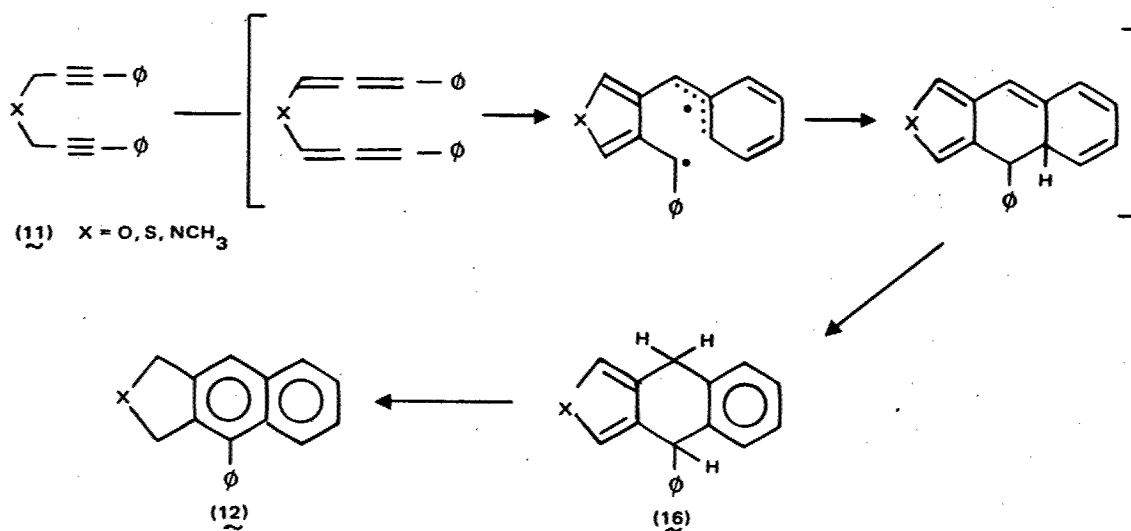
In the case of 11 (X = NCH₃), two isomeric dimers of gross structure 17 (R = phenyl) form beside 12 (X = NCH₃) and 16 (X = NCH₃).

8
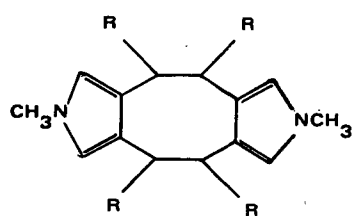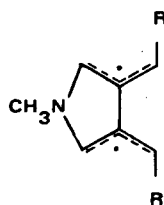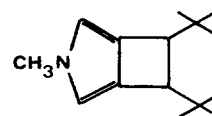
(17) R = φ, H, tBu   (18)   (19)

The dimers are generated by dimerization of the diradicals 18. When steric hindrance precludes dimerization, e.g., R = tBu, the bicyclic compound 19 is formed.

The significance of the bisallene intermediate has been substantiated by the isolation of 20 and 21 (Reference 18). It is interesting to note that
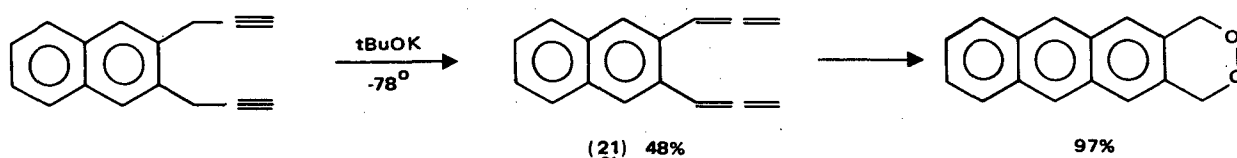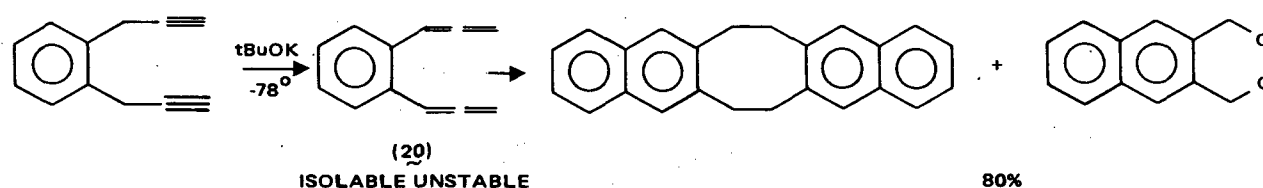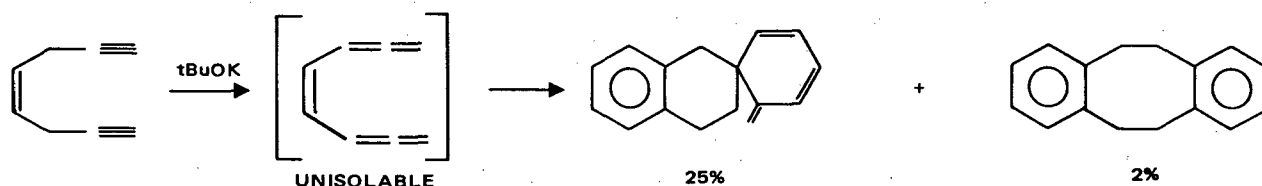
thermolysis (no base involved) of these propargylic systems could conceivably generate the bisallene intermediates but has not been reported. A very

9

closely related system 22 undergoing thermolysis via a bisallene is known (Reference 19) (vide infra).

(22)
R = H, D
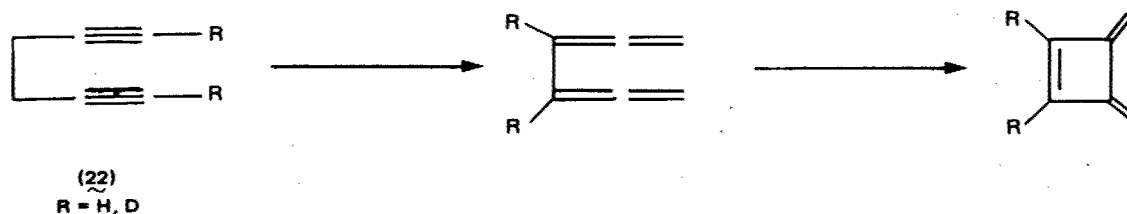
In warm acetic anhydride, propiolic acid 23 forms the anhydride which undergoes intramolecular cyclization to a phenylated naphthalene derivative (Reference 20a). Similar reactions have also been reported of acid anhydrides (References 20b and c), amides (Reference 21) and esters (Reference 22).

REF 20a

(23)

52%

REF 20b

71%

$AR - \equiv - CO_2H$ $\longrightarrow$ REF 20e

$AR =$

AC$_2$O
Δ
REF 21

$HC \equiv C - \overset{O}{\underset{\|}{C}} - O \rightarrow CH_2 - \equiv - Ar$
AC$_2$O
Δ
REF 22
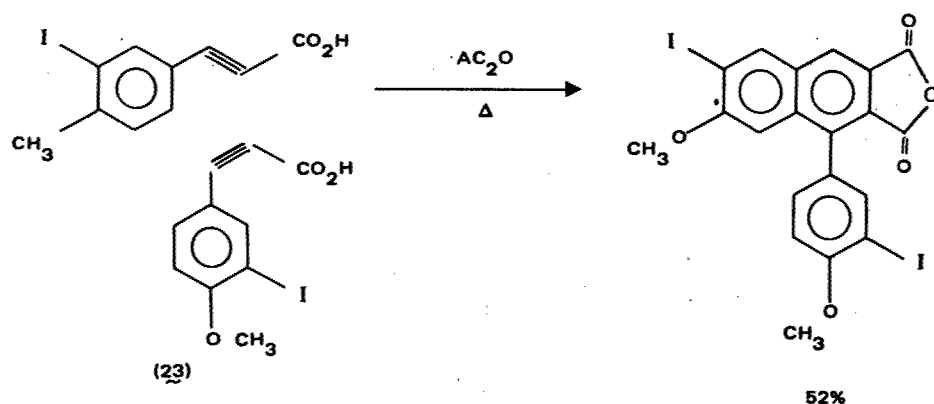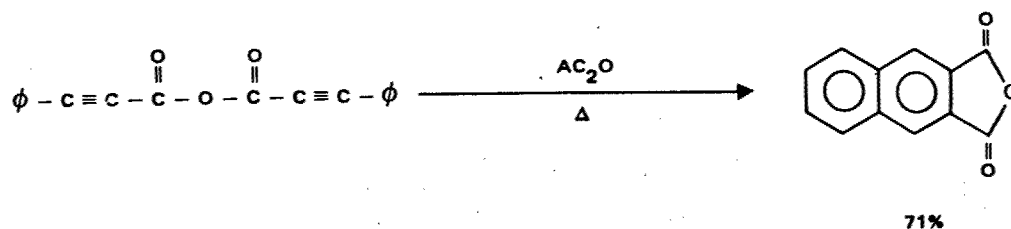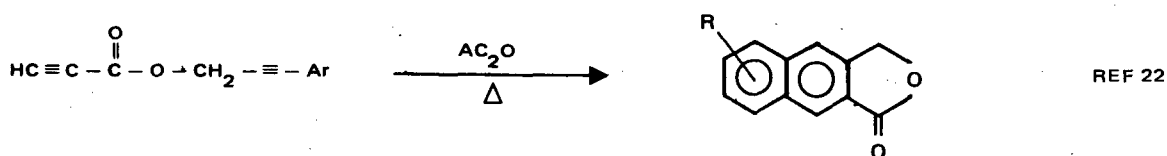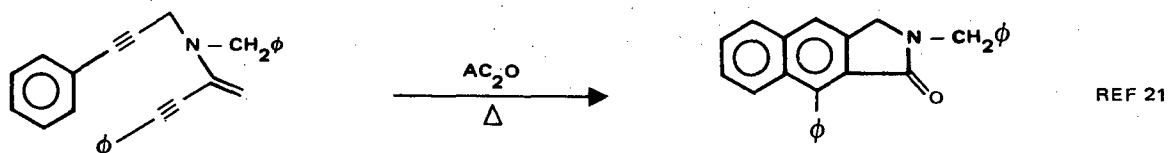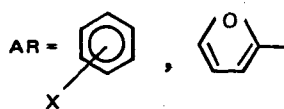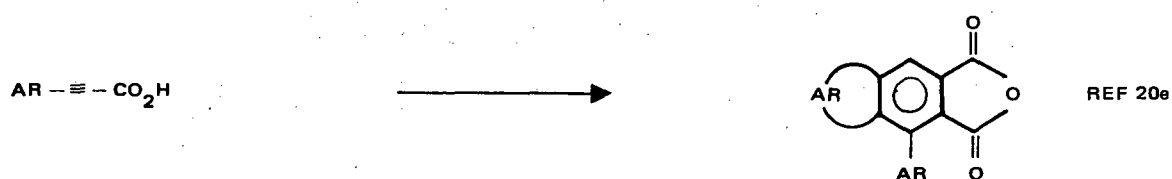
In a study (Reference 23) on the total synthesis of gibberellic acid, intramolecular cyclization of the model compound $\underset{\sim}{24}$ has been demonstrated to occur in acetic anhydride. Other types of intramolecular cyclization are known to take place in various acidic media (Reference 24).

(24)
135°
AC$_2$O
70%
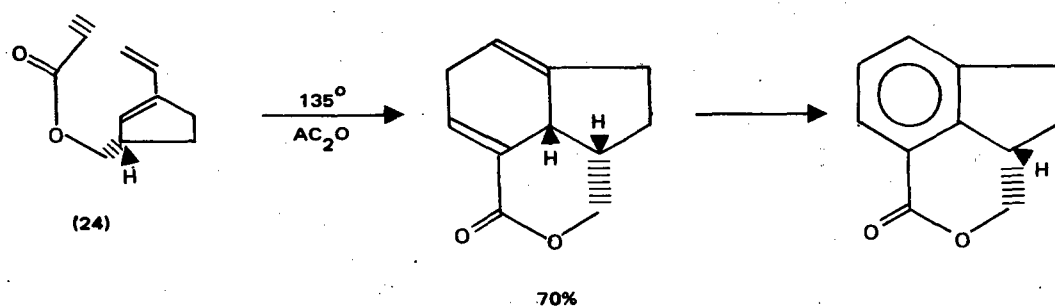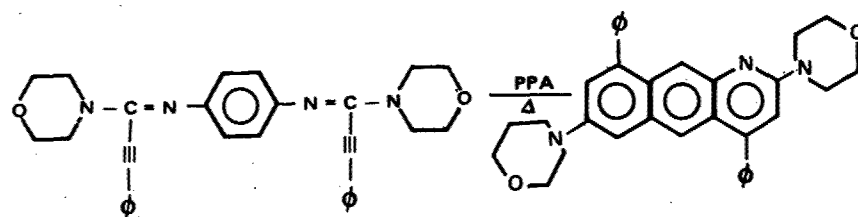
REF 24a

REF 24b

REF 24e

$R_1R_2 = H, \phi$
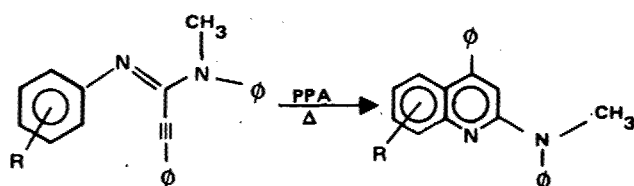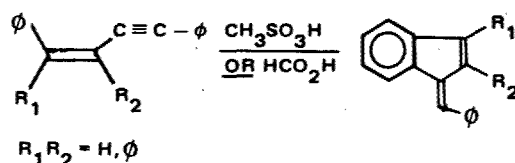
Enynes undergo intramolecular cyclization upon irradiation (Reference 25). No volatile materials are evolved and the end products are stable cyclic compounds, mostly aromatic.
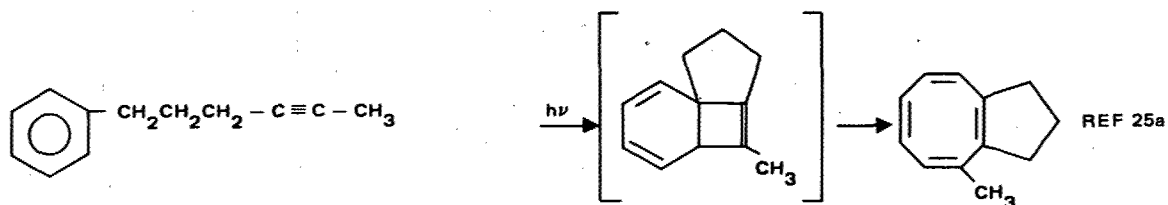
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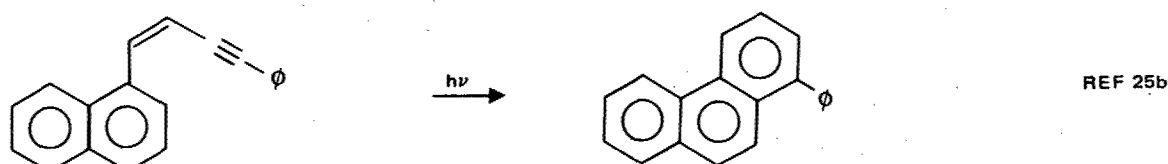
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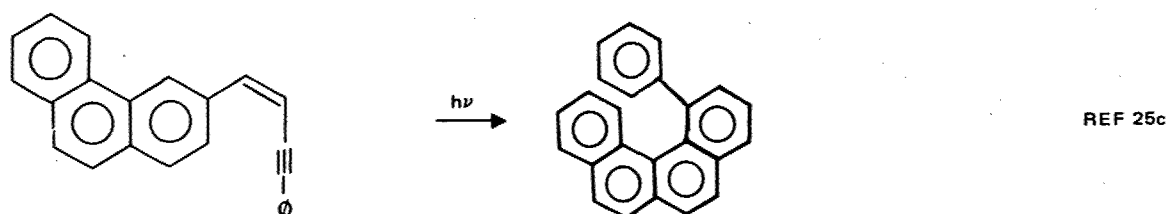
REF 25c

In the conjugated enyne systems, photocyclization takes place in the singlet excited state, as indicated by the lack of influence of triplet sensitizers and quenchers. The $\underline{trans}$ geometry of acetylenes in the first singlet state also facilitates reaction. It is noteworthy that the cyclization reaction does not proceed thermally. Presumably, energy dissipation from the hot ground state occurs by a different mode, e.g., a facile $\underline{cis}$-$\underline{trans}$ isomerization at the double bond ($\underline{vide}$ $\underline{infra}$: Section IIB).

Activation of acetylenic compounds by organometallic catalysts to undergo $\underline{inter}$- and $\underline{intramolecular}$ cyclization is well-known (Reference 26). Terminal acetylenes form alkylbenzenes in the presence of a cobalt complex (Reference 27). Organocobalt also catalyzes co-trimerization of organic
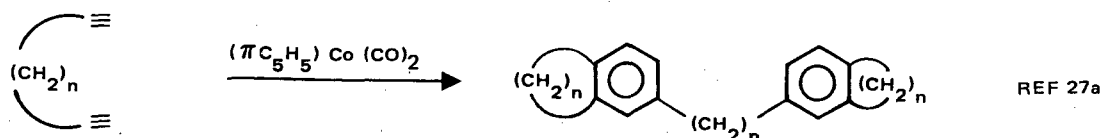
nitriles and terminal acetylenes.
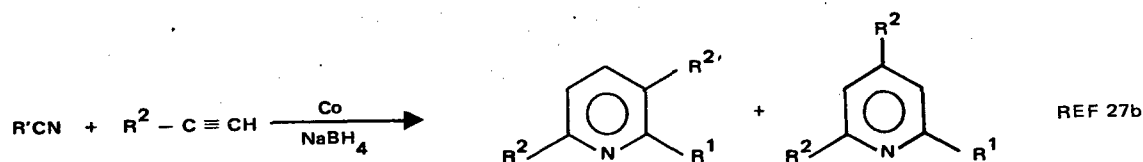
Likewise, rhodium, palladium and copper are known to catalyze $\underline{inter}$- and $\underline{intramolecular}$ cyclization of acetylene compounds to give heterocycles (Reference 27). Some representative examples are given below.

13

$[(C_2H_4)_2 RhCl]_2$ REF 27c

$2\ CH_3-C\equiv C-CH_3$

$(\phi CN)_2\ Pd\ Cl_2$ REF 27d

OH

OH

$(\phi CN)_2\ Pd\ Cl_2$ REF 27d

ϕ

$CH_3\ C\equiv C - \overset{R}{\underset{O\ R^1}{\underset{|}{\overset{|}{C}}}} - CH_2\ OH \xrightarrow{\ CuCl\ }$ REF 27e

CH_3

R

$\equiv - \equiv - \overset{R}{\underset{R}{\overset{|}{\underset{|}{C}}}} - OH \xrightarrow{\ CuCl\ }$ REF 27f

OH

$\equiv - \overset{R}{\underset{R}{\overset{|}{\underset{|}{C}}}} - OH$
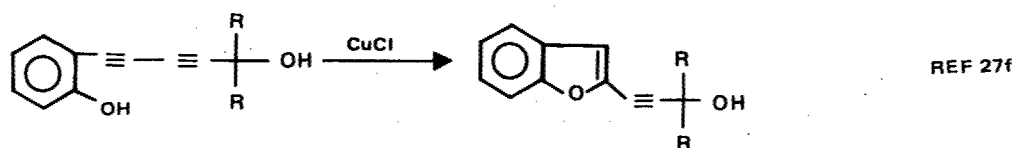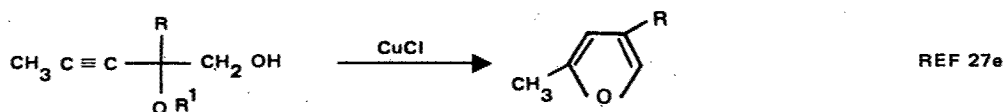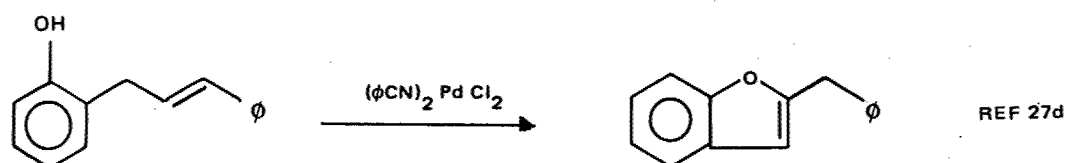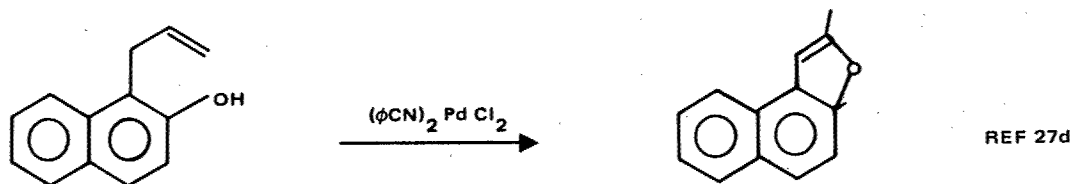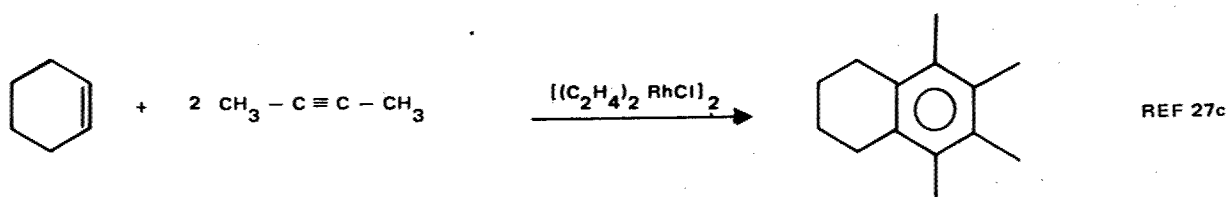
At high temperatures, aluminum oxide and silica gel also catalyze intramolecular cyclization. Stable heteroaromatic cyclic compounds have been formed (Reference 28).

CH_3

$\xrightarrow[550°]{SiO_2}$ REF 28a

$N = CH\phi$

N
H

ϕ

14
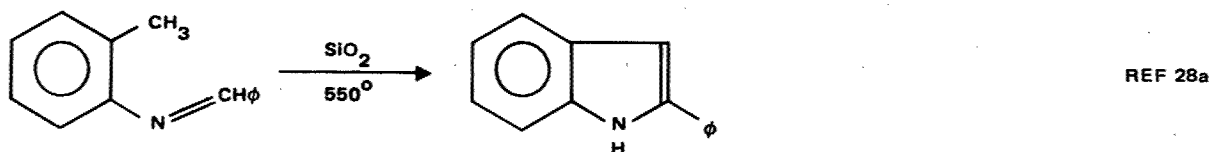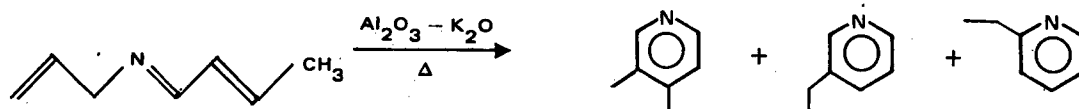
Thermally-induced intramolecular cyclization has been studied as an important route to generate aromatic and heteroaromatic nuclei. In certain cases, elimination of small molecules serves as the driving force for cyclization and aromatization. In the other cases, no volatiles are produced.

At high temperatures, o-hydroxyacetophenone cyclizes to give benzofuran after elimination of water (Reference 29a). Similar cyclization-elimination reactions afford substituted pyrroles (Reference 29b), benzoquinolines and benzoisoquinolines (Reference 29c).
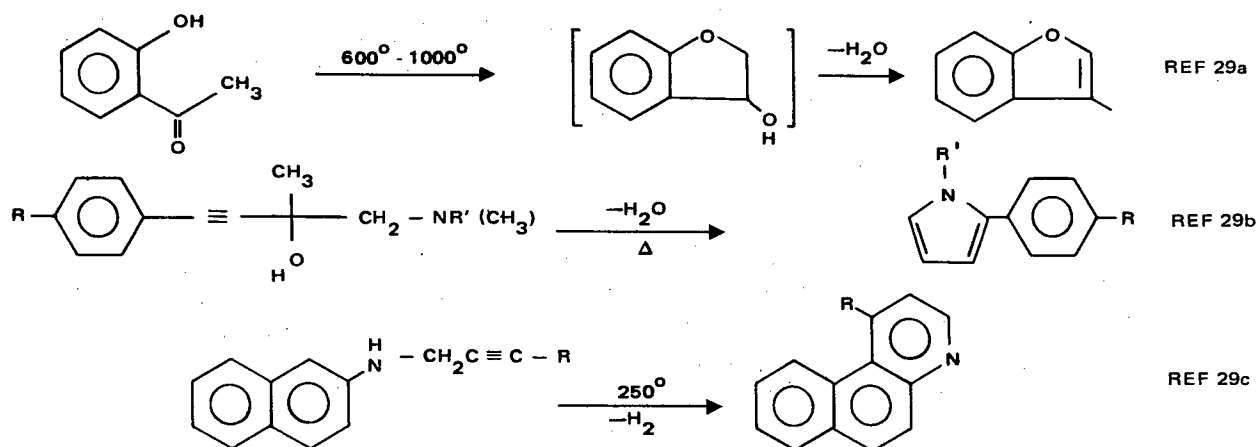
An efficient procedure to construct aromatic nucleus takes advantage of the facile thermal cyclization of hexatrienes. The positioning of the dimethylamino group in the 1-position sets the stage for aromatization of the resulting cyclohexadiene _via_ the elimination of dimethylamine (Reference 30). Application of this procedure has led to various aromatic and heteroaromatic systems.

15
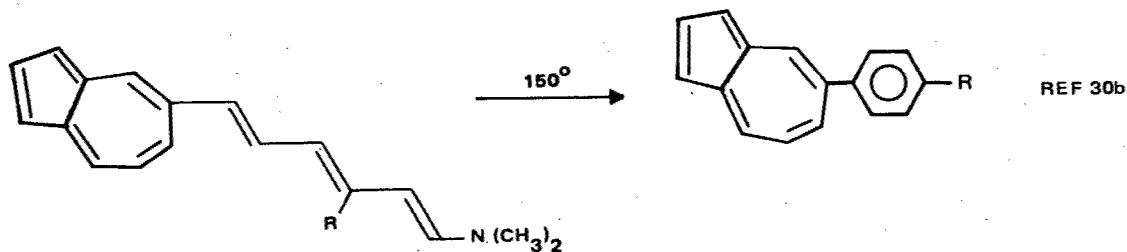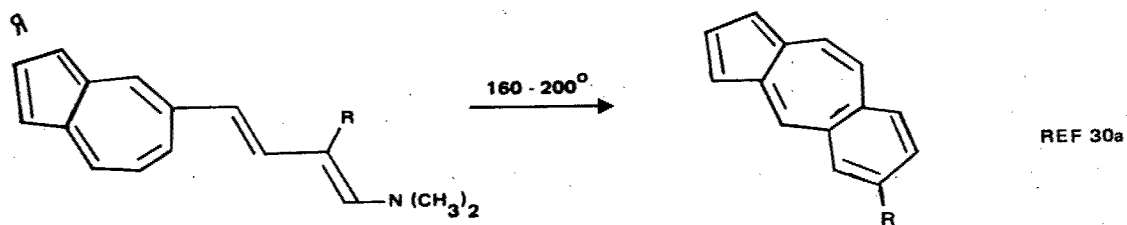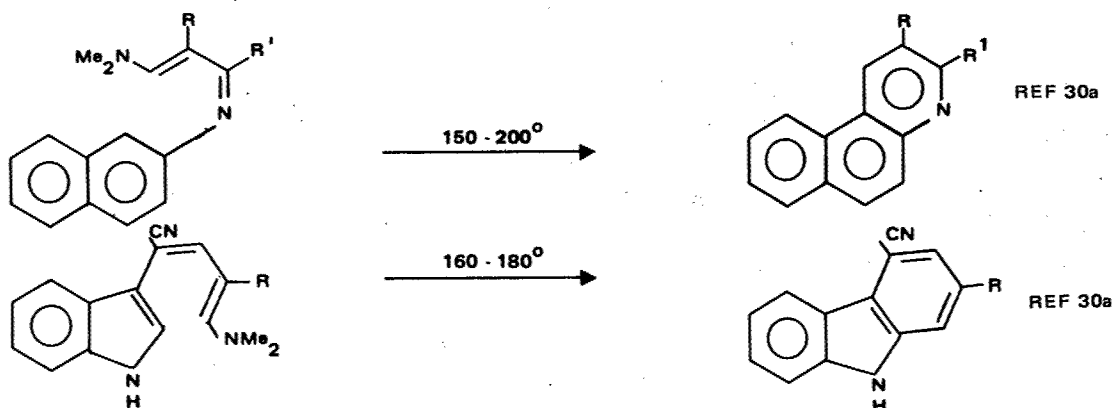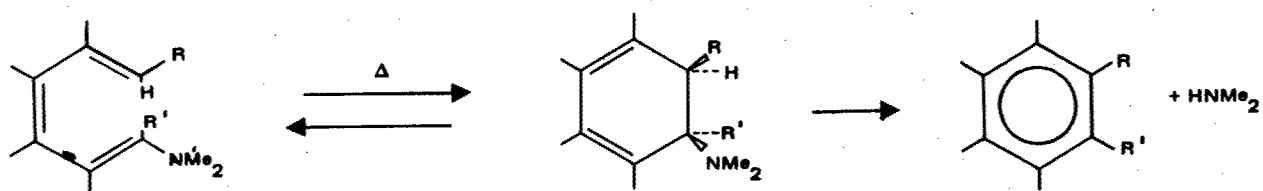
Under gas-phase pyrolytic conditions, conjugated and non-conjugated ene and yne systems undergo cyclization. For example, pyrolysis of 25 yields a mixture of quinoline and isoquinoline (Reference 31).
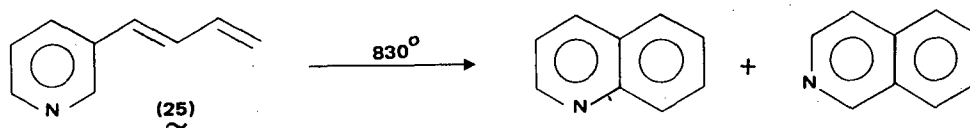
Flash vacuum pyrolysis of o-ethynylbiphenyl 26 is mechanistically interesting. Isolation of benz[b]azulene 27 suggests strongly the intervention of a vinylcarbene intermediate (Reference 32a). The result parallels that obtained under carbene-generating conditions (Reference 32b).
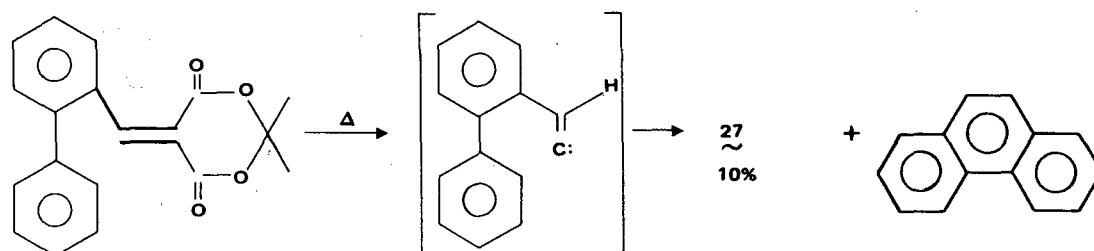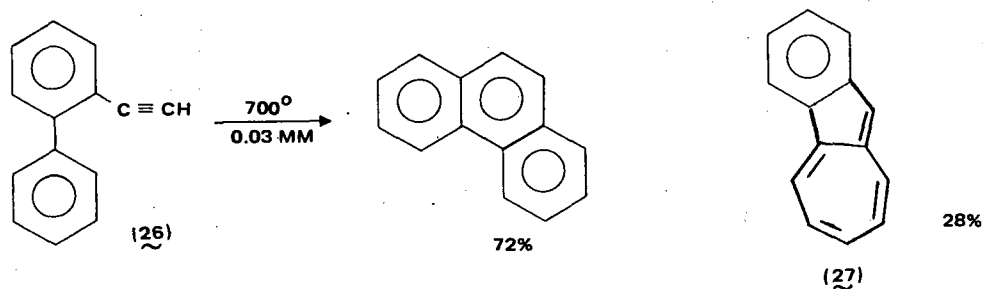
Bisallene intermediates are mechanistically significant in the base-catalyzed cyclization of bispropargylic compounds (vide supra) (References 15 through 19). Thermal rearrangements of other bispropargylic compounds are also best described by the intervention of bisallenes (Reference 33) whose importance has been established by the synthesis and thermal cyclization of the bisallene 28 (Reference 34).
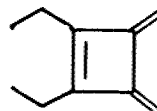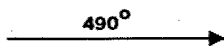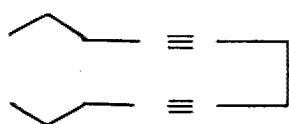
REF 33a
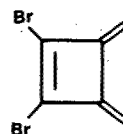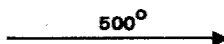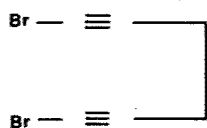
REF 33b

REF 33c

REF 33d

MINOR   MAJOR

(28)   100%
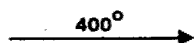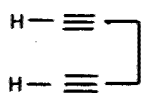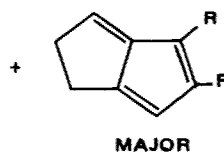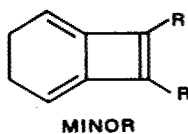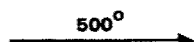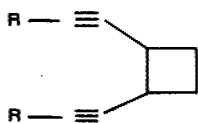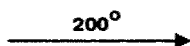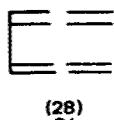
Bispropargyl compounds with extended conjugation at the triple bonds undergo thermal intramolecular cyclization reactions affording fused aromatic nuclei. The conversions of 7 to 8 and 9 to 10 are catalyzed by weakly basic

18

(7)	$R_3 = CH_3$, $R_4 = VINYL$	(8)	$R_3 = CH_3$, $n = 0$
(9)	$R_3 = CH_3$, $R_4 = \phi$	(10)	$R_3 = CH_3$, $n = 4$
(29)	$R_3 = R_4 = ARYL$	(30)	$R_3 = \phi$, $n = 4$
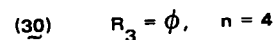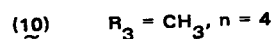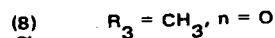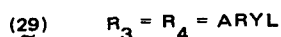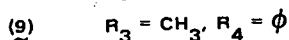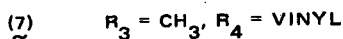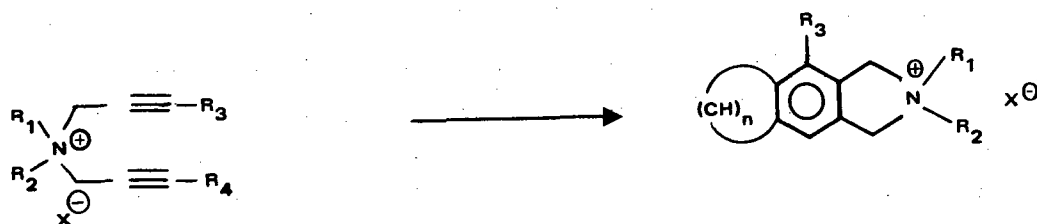
media (vide supra) (Reference 15) but the bis-arylpropargyl compounds 29 cyclize in hot water to give the naphthalene derivatives 30 (Reference 35). Propargyl ethers of phenylacetylenic and vinylacetylenic alcohols are also converted to phthalans upon heating in xylenes (Reference 36). Mechanistic-ally, these reactions may proceed via a six-centered transition state akin to

$$130 - 160^{\circ}$$
XYLENE

REF 36

R = ALKYL, H
R_1 = ALKYL, H
R_2 = ALKYL, H
$R_1 R_2$ = —CH = CH — CH = CH —
R_3 = ALKYL, H
R_4 = ALKYL
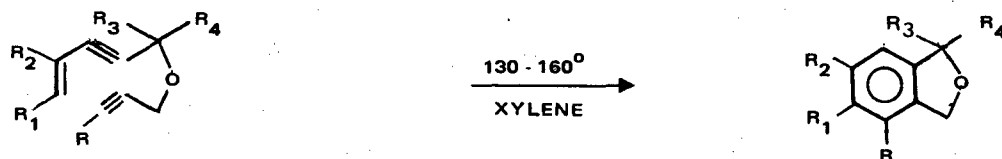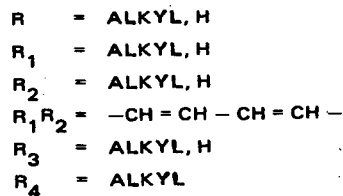
the Diels-Alder reaction. In the light of the bisallene mechanism substantiated for thermal cyclization reactions of other bispropargyl compounds, a similar mechanism may also operate. An interesting and mechanistically analogous
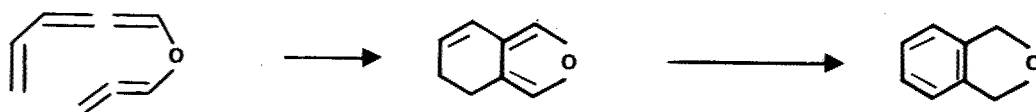
intermolecular reaction is the thermal dimerization of phenylallene (Reference 37), a naphthalene derivative being generated.
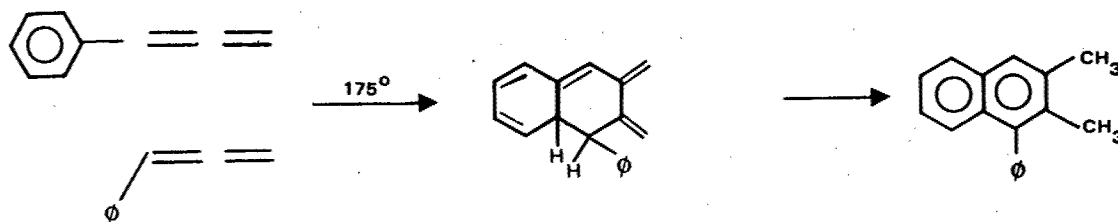
Certain reactive conjugated ene and yne systems undergo thermal intramolecular closure at ambient temperatures. The bis-fulvalene 31 (Reference 38) cyclizes to give 32 at 30°. Although orbital symmetry arguments suggest a _trans_ disposition of the two bridgehead hydrogens, nmr coupling constants do not provide unambiguous substantiation. The aromatization of 32 is a facile symmetry-allowed thermal reaction.

REF 38

(31)   (32)
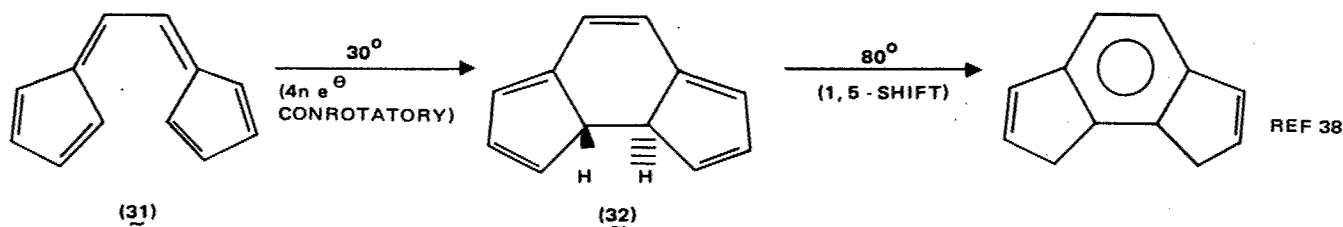
The unstable <u>cis</u>,<u>cis</u>-3,5-octadiene-1,7-diyne (33) is rapidly converted into benzocyclobutadiene dimer in 85% yield (Reference 39). The cyclic bisallene 34 is a highly possible intermediate which thermally rearranges to benzocyclobutadiene.
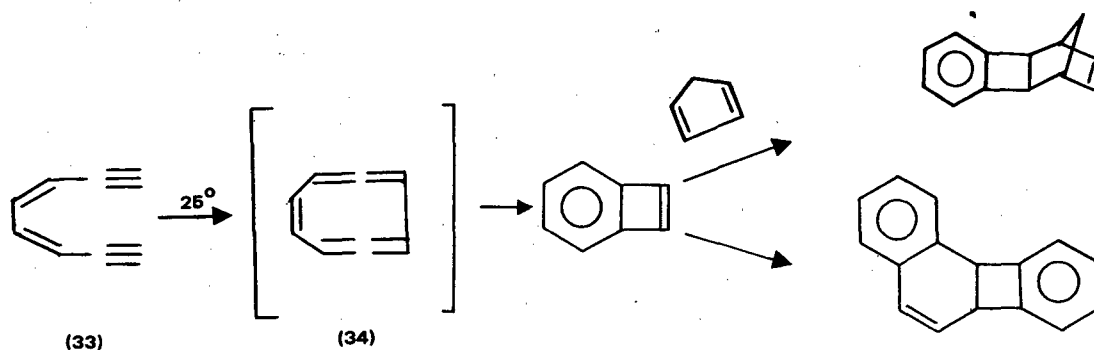
An interesting comparison to the facile thermal closure of 33 is the formation of benzene from <u>cis</u> and <u>trans</u>-1,3-hexadien-5-yne 35 under pyrolytic conditions (Reference 40), product yield being 25-36% at 274° and 50% at 510°. A complex high-boiling mixture accompanies benzene formation.
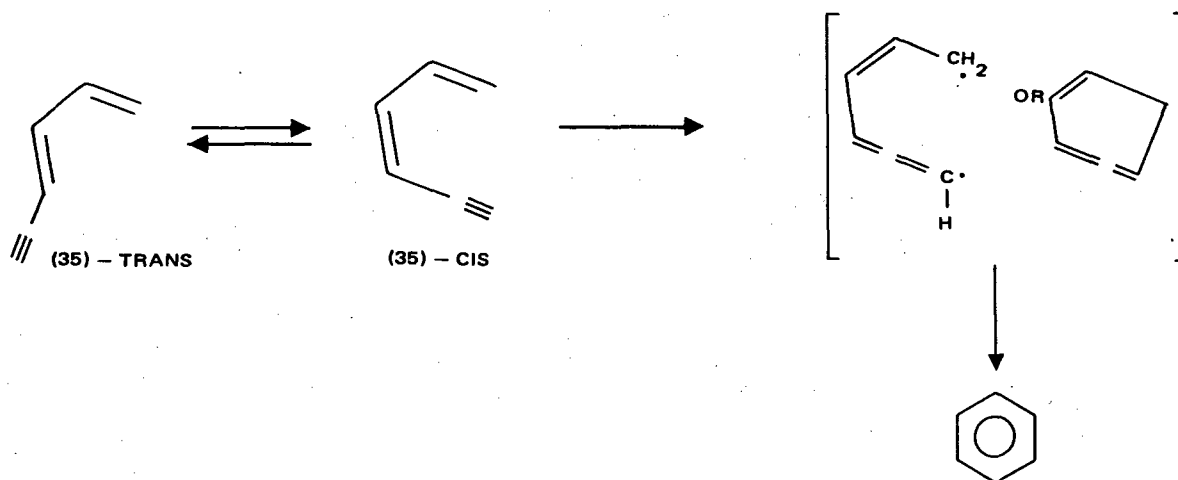
o-Bis(phenylethynyl) Compounds

Extensive research has been carried out in the synthesis and chemical behavior of compounds having <u>ortho</u>-positioned phenylethynyl pendants. Structurally, these compounds can be categorized into four classes: the aromatic and heteroaromatic keto-diynes (36), the cyclobutene-<u>trans</u>-diynes (37), bistolane derivatives of phosphorus, silicon and sulfur (38) and the bis(phenylethynyl) aromatics (39, 40, 41, 42).

(a)   (b)   (c)
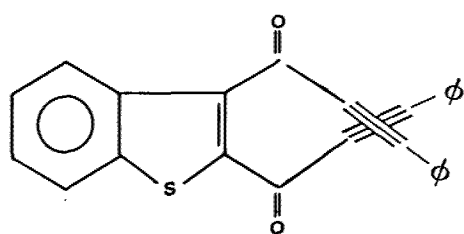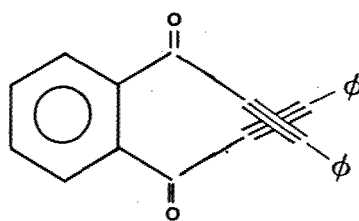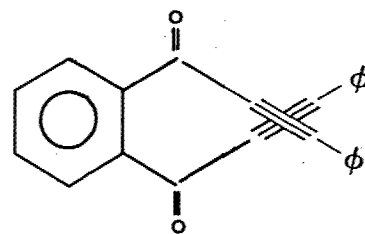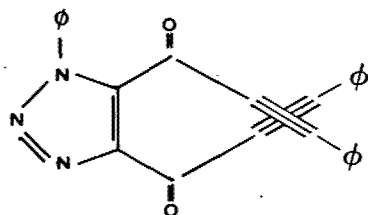
(d)   (36) (e) X = Nφ   (g)
              (f) X = O
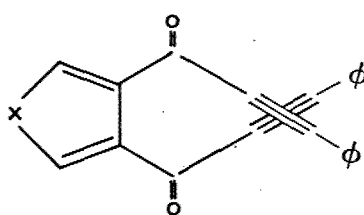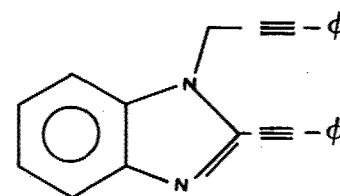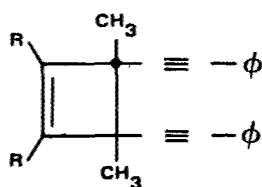
(37) (a) R = CH₃
      (b) R = φ
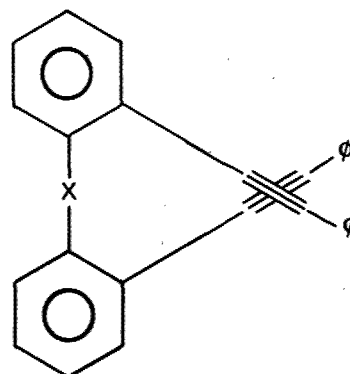
(38) (a) X = P—φ
      (b) X = SiMe₂
      (c) X = SO₂

22
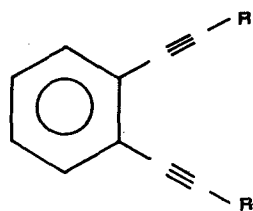
(39) (a) R = H
      (b) R = CH$_3$
      (c) R = ϕ
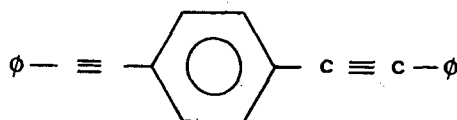
(40)
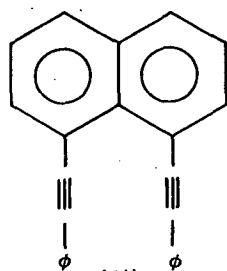
(41)
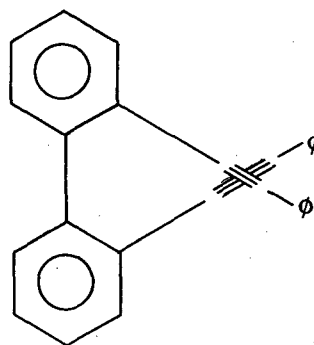
(42)

The keto-diynes 36 follow a uniform reaction pathway with chlorotris-(triphenylphosphine)rhodium[I] to yield the rhodocyclopentadienes 43, 44 and 45 which are key intermediates in the synthesis of various fused ring systems (References 41a through i).

(36)

$RhL_3Cl, L = P\phi_3$

(43)

FROM (36b)

280-290°

30%

O, S, Se

ϕNO

$RC \equiv C-R$

X = O, S, Se, Te

R = ϕ, CO_2CH_3

(36a)   AR   =   REF 41a

(36b)   REF 41b, c

(36d)   REF 41d

(36e)   REF 41e

(36f)   REF 41f

24

(36c) (44) $R = \phi, CO_2CH_3$ REF 41g

RhL₃Cl, L = Pϕ₃ RC≡CR

(36g) (45) REF 41h, i

RhL₃Cl

RC≡CR

CO

O, S, Se

X = O, S, Se
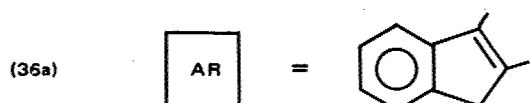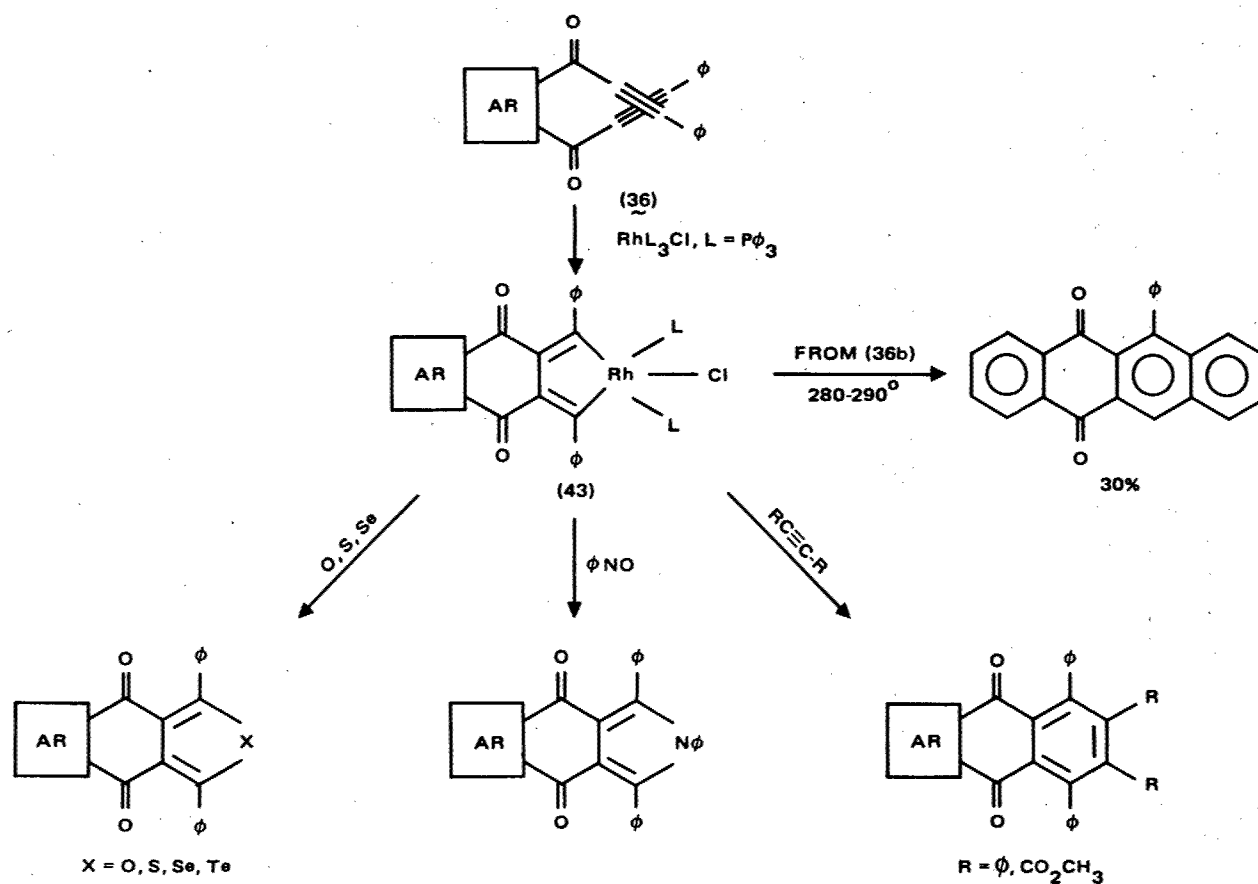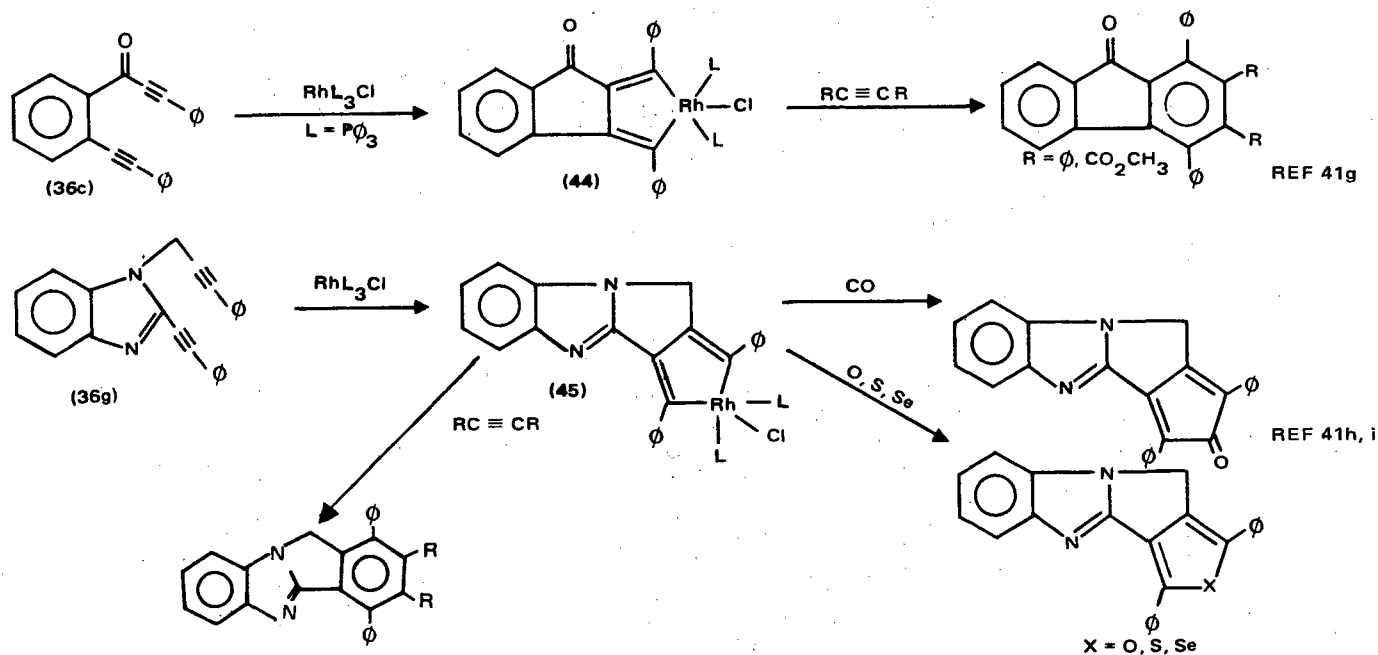
The organonickel chemistry of keto-diyne 36b and its benzo analog 46 has been studied. Dimeric compounds are produced by catalysis of nickel[0] tetracarbonyl (Reference 42).

(36b) Ni(CO)₄, 20° 80% + 2%

(46) Ni(CO)₄, 20° 38% + 43%
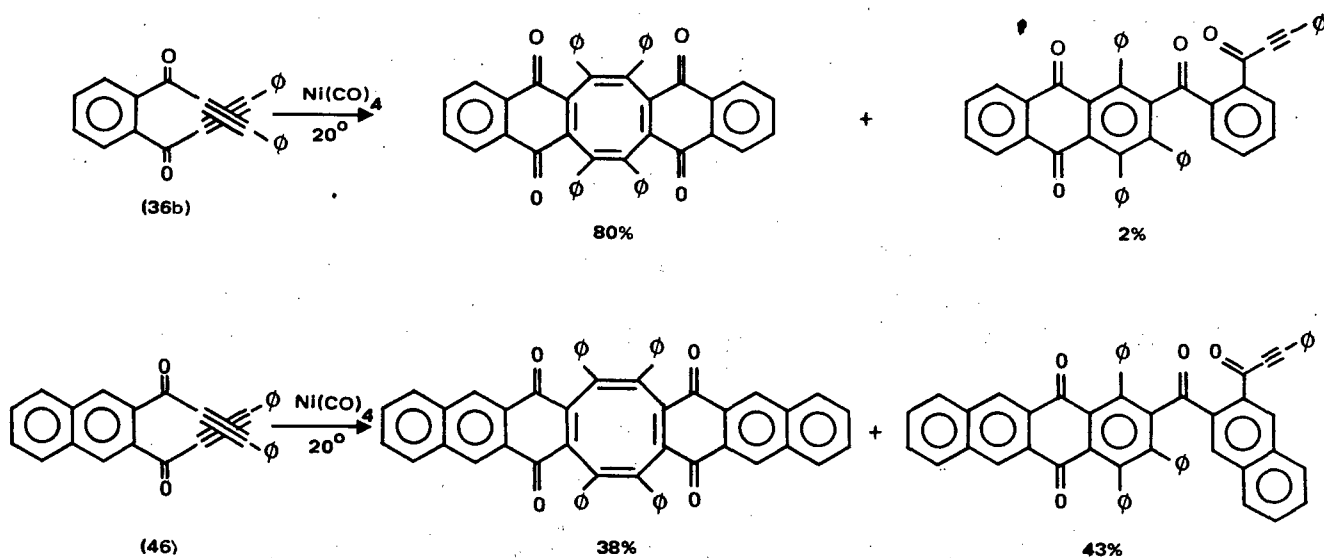
Either organonickel complex (47a or b) could be the active species in the catalytic conversion of 36b to its dimers. Trapping of the intermediate with reactive acetylenes leads to the isolation of 48.

(47a)   (47b)   (48)   R = R$_1$ = ϕ
                                      R = ϕ, R$_1$ = ϕC̈
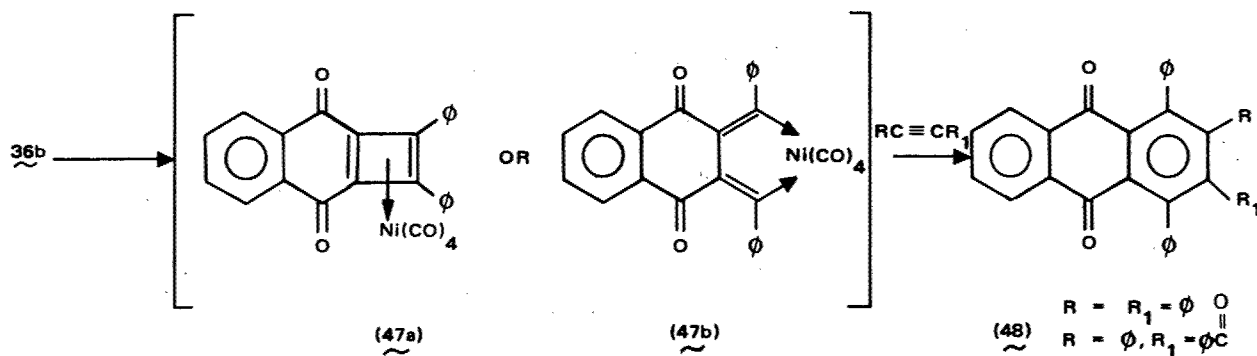
It is interesting to note the isolation of the fused aromatic system 49 in 1% yield from a benzene solution of 36b after prolonged standing at room temperature. The possibility of a thermally induced intramolecular cyclization of 36b has been realized (Reference 43). (The analogous reaction with

(36b)   (49)   64%
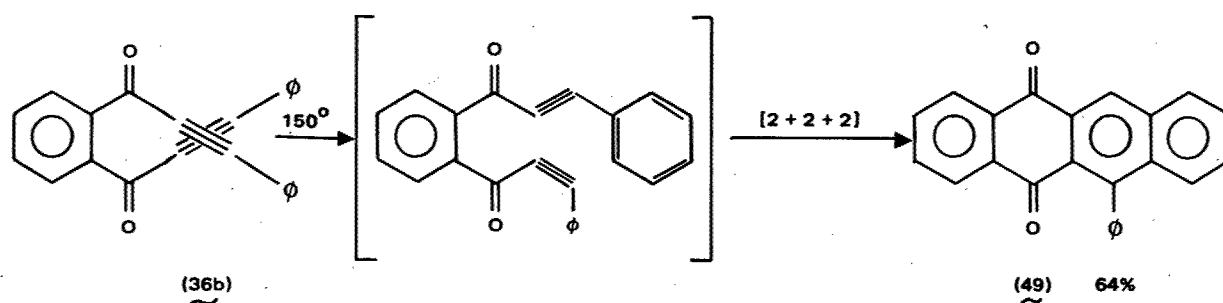
o-bis-phenylpropargyl benzene also takes place (Reference 43)). Irradiation of 36b similarly gives 49. The mechanism proposed for the photochemical reaction involves an initial formation of the reactive cyclobutadiene by a [2+2]

26

cycloaddition followed by ring cleavage to the diradical which undergoes rearrangement and then recombination.
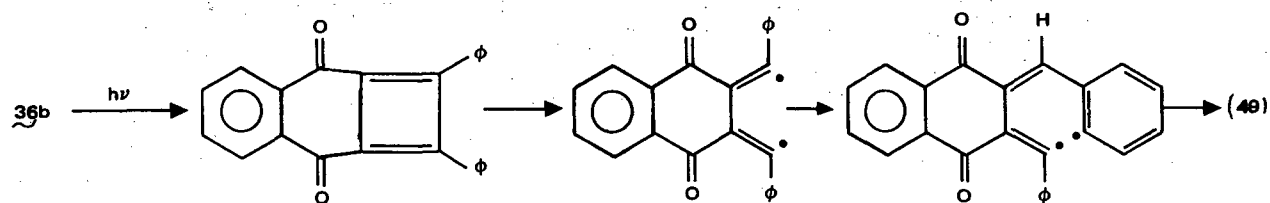
The cyclobutene-<u>trans</u>-diynes 37 undergoes cycloaddition reaction with reactive acetylenes either thermally (References 44a through c) or by the catalytic action of chlorotris(triphenylphosphine)rhodium [I] (Reference 44c). In the absence of acetylenes and the rhodium complex, a dimeric compound is formed (Reference 44d). Compound 50 has been established
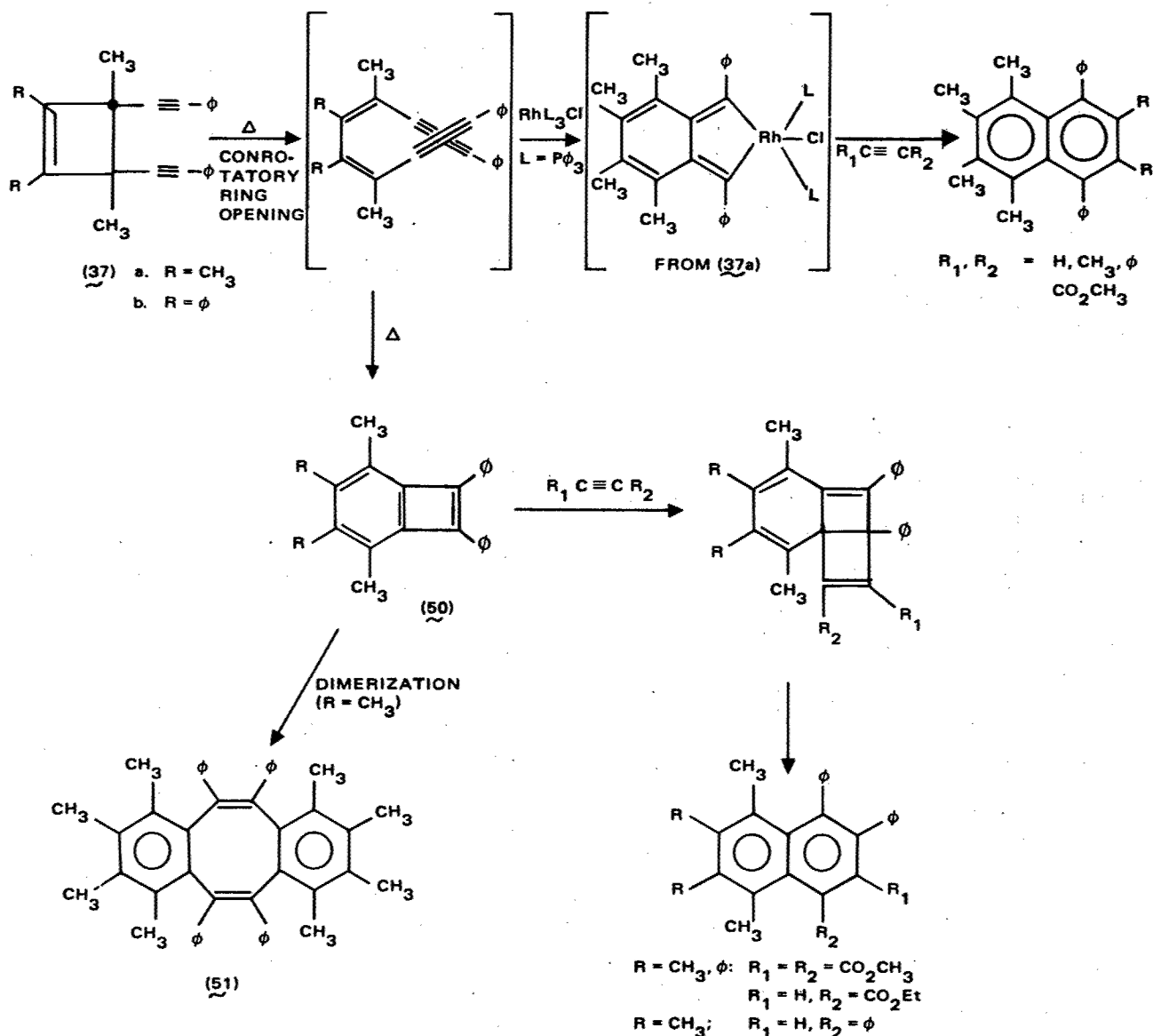
to be the precursor of the dimer 5̲1 by its successful isolation (Reference 44d) and thermal conversion to 5̲1.

Bis-tolane derivatives of phosphorus, silicon and sulfur (3̲8) are interesting in their resemblance to 3̲6, having criss-crossing phenylethynyl substituents. While the organorhodium chemistry of the sulfur compound 3̲8c (Reference 45a) parallels that of keto-diynes 3̲6, the phosphorus analog 3̲8a undergoes complexation with chlorotris(triphenylphosphine)rhodium [I] to yield a novel cyclobutadiene-rhodium[I] complex 5̲2 (Reference 45b).

28
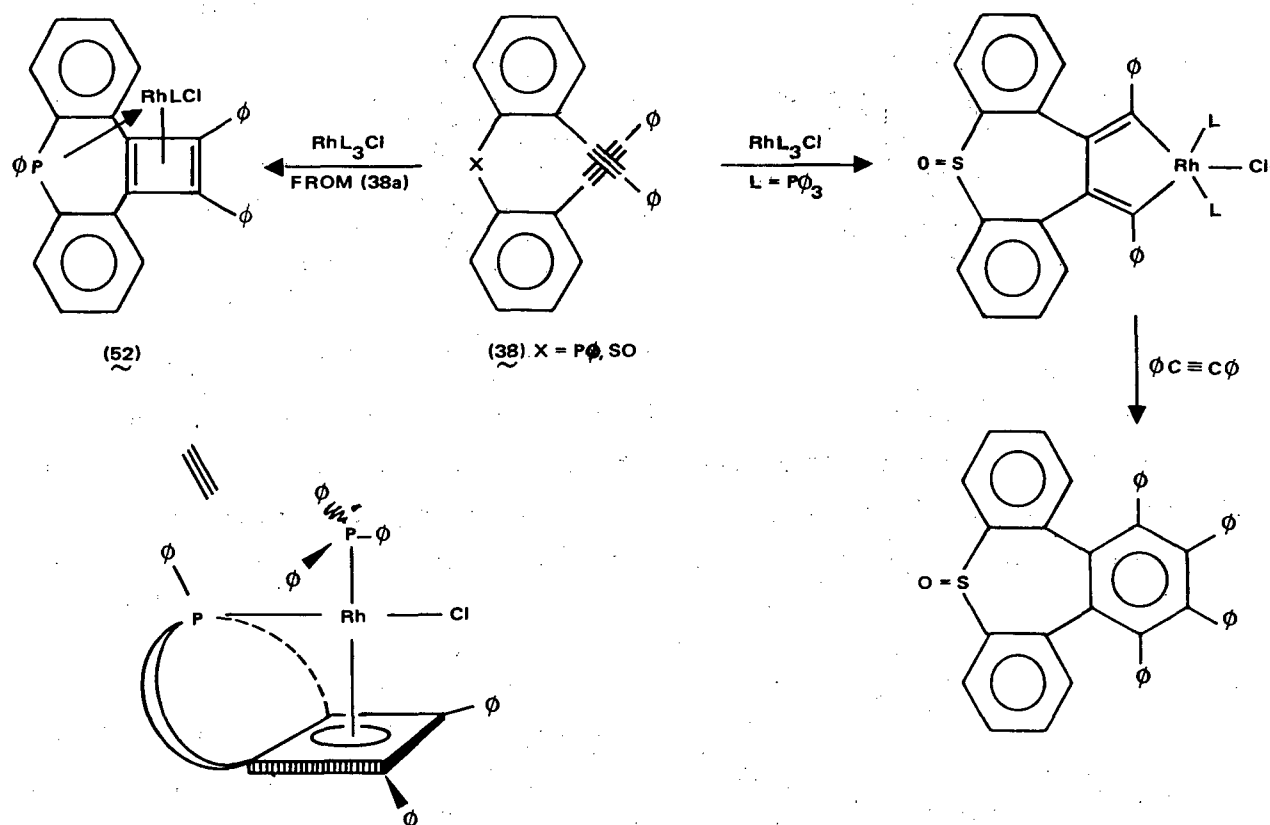
Both 38b (Reference 45c) and 38c (Reference 45a) yield substituted azulenes in the presence of an organopalladium complex. The structure of the cyclobutadiene-palladium complex initially formed during the reaction is inferred both from the trapping experiment with diphenylacetylene and azulene formation.
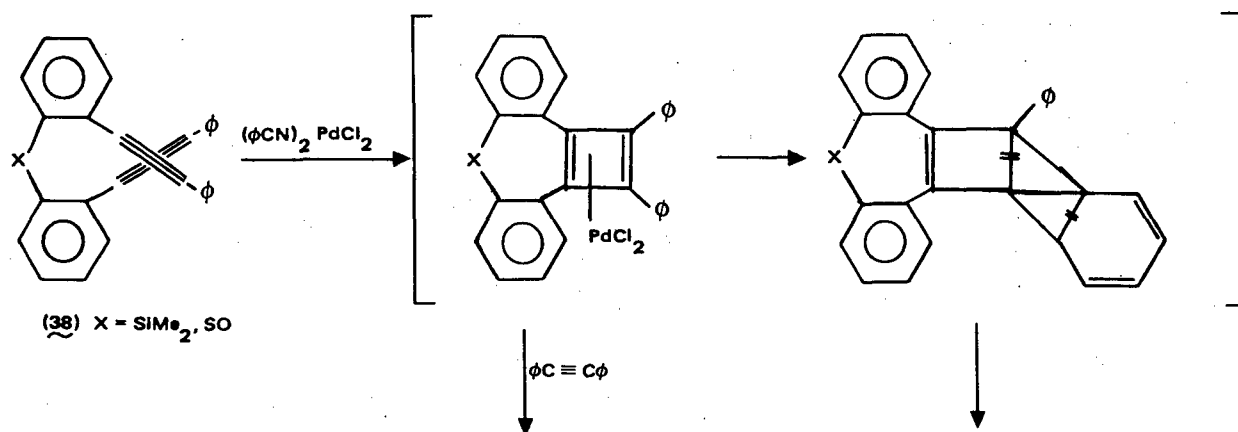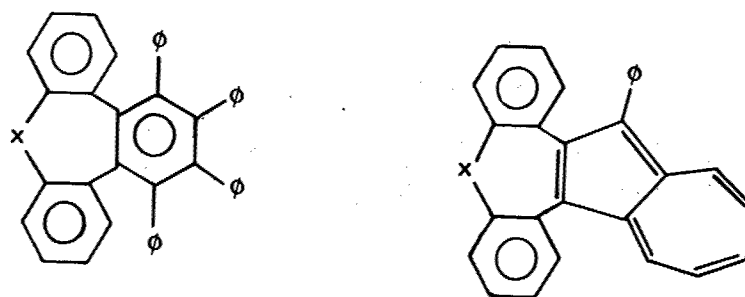
Thermal cyclization studies of 38 have not been reported. An inter-
esting rearrangement-cyclization reaction (Reference 45d) of 38a occurs upon
irradiation, however. The structure of the photochemical product 53 has
been established by an X-ray study of its methyl iodide salt.
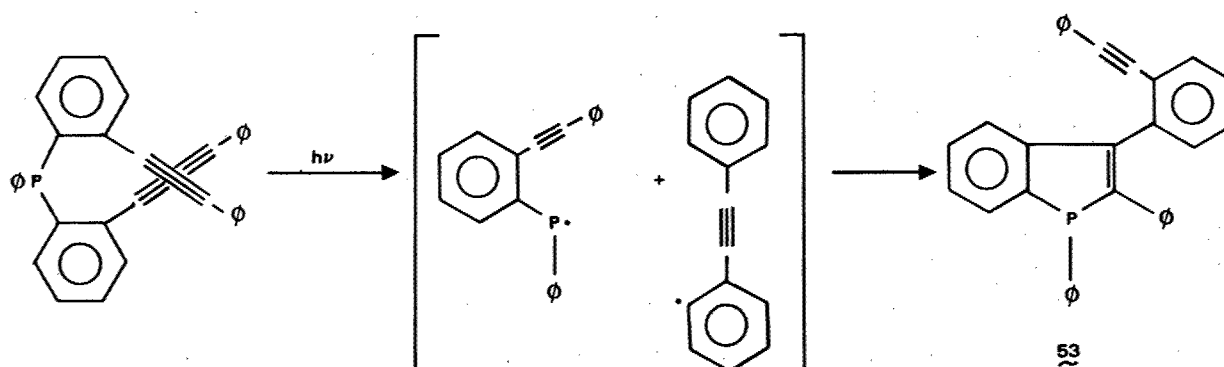
The bis(phenylethynyl) aromatics (39-42) have been studied for their
different modes of cyclization under thermal, photochemical and organo-
metallic conditions.

a. R = H
(39) b. R = CH₃
c. R = φ
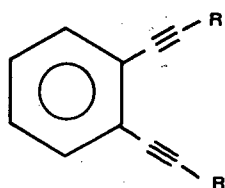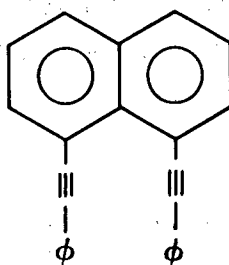
ANGULAR
(41)
PARALLEL
(42)
CRISS-CROSS
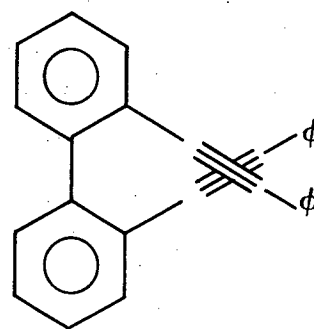
Although the thermal behavior of 39a and 39b is not known, 39c appears to be stable in refluxing benzene and dimethylformamide (Reference 46). Irradiation of 39a and 39b results in the formation of isomeric azulenes (Reference 46b).

(39) R = H, CH₃

AND

31
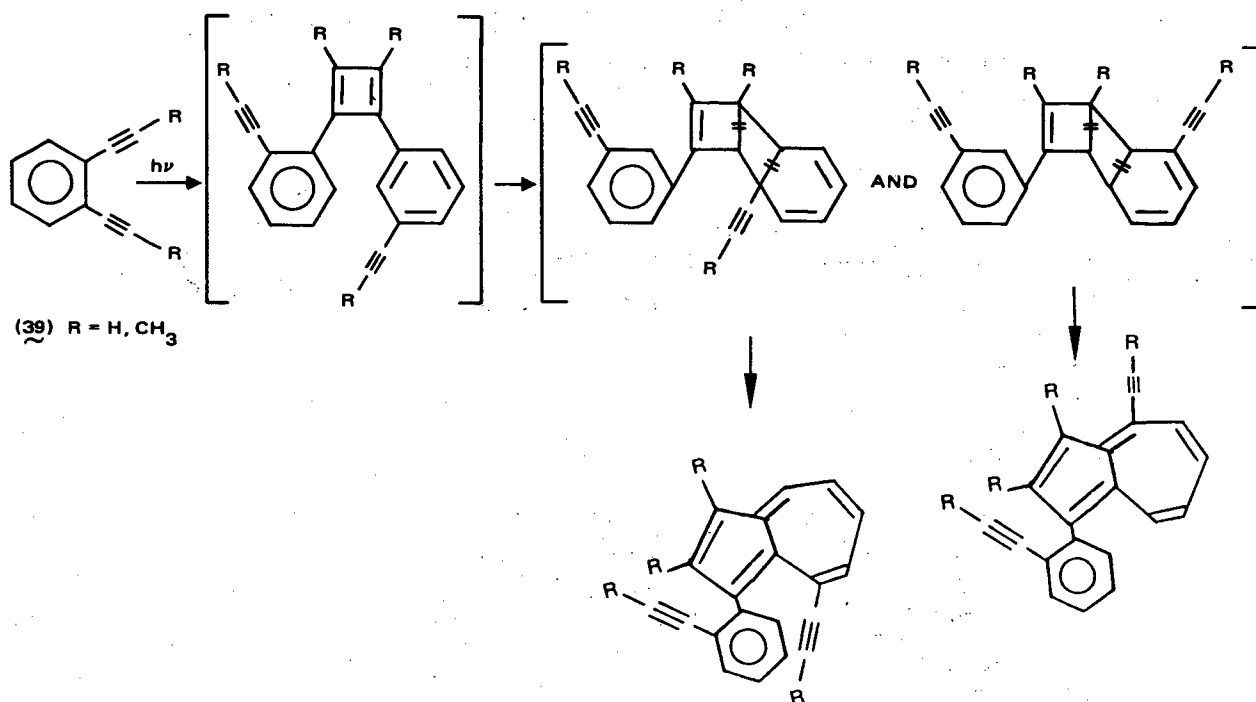
The proposed mechanism is the conventional cyclobutadiene formation. Irradiation of 39c yields the blue-green dimer "Verden" besides polymeric materials. The structure of "Verden" is proposed as 54 based on available chemical and physical properties (References 46a and c). A likely intermediate is 55.

(39c)　　　　　　　　　　　　(55)　　　　　　　　　　　54 "VERDEN"
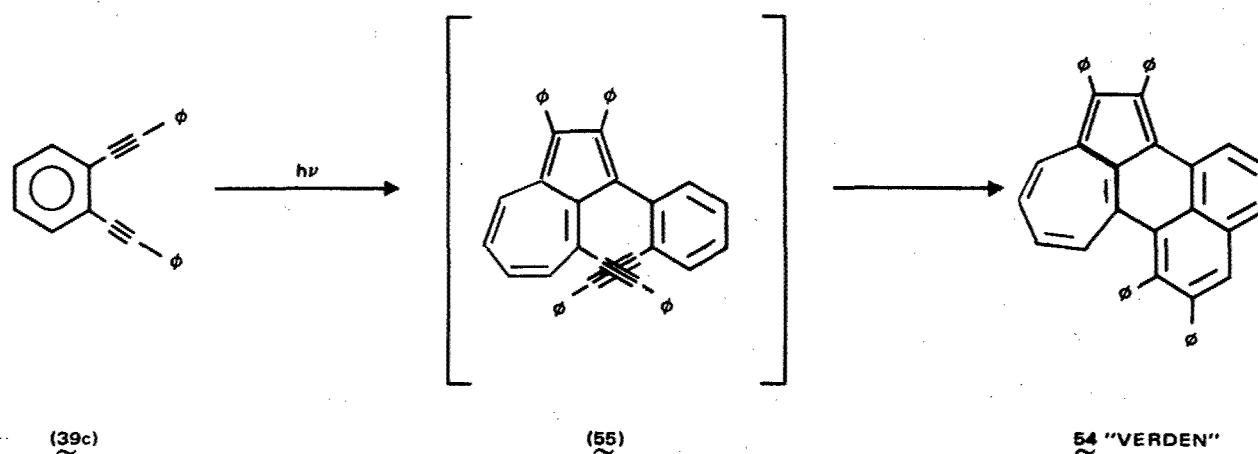
Similar photochemical reactions of the para-isomer (40) of 39a, c have been reported (Reference 46d). Although the azulene
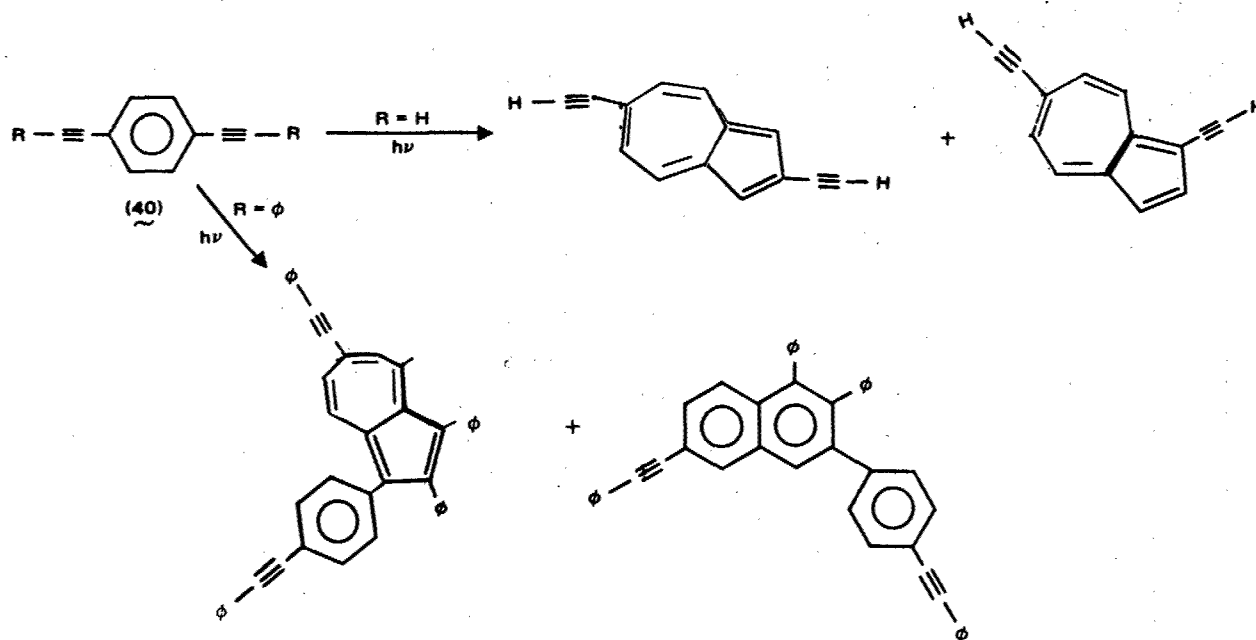
products are unequivocally characterized, the naphthalene derivative is indistinguishable from the isomeric structure 56.

(56)
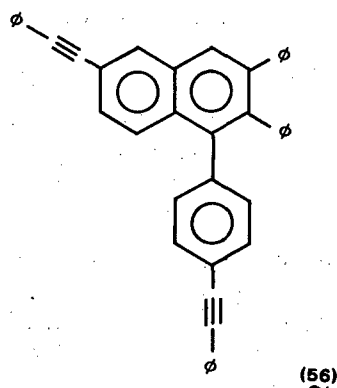
Both thermal and photochemical transformations of 1,8-bis-(phenylethynyl)napthalene (41) have been examined in detail. Three research groups have provided comparable results from independent studies (References 46a, 47a through e).

(57)

(58)

(41) R   = H, CH₃
      R₁ = H, CH₃, OCH₃
      R₂ = H, CH₃
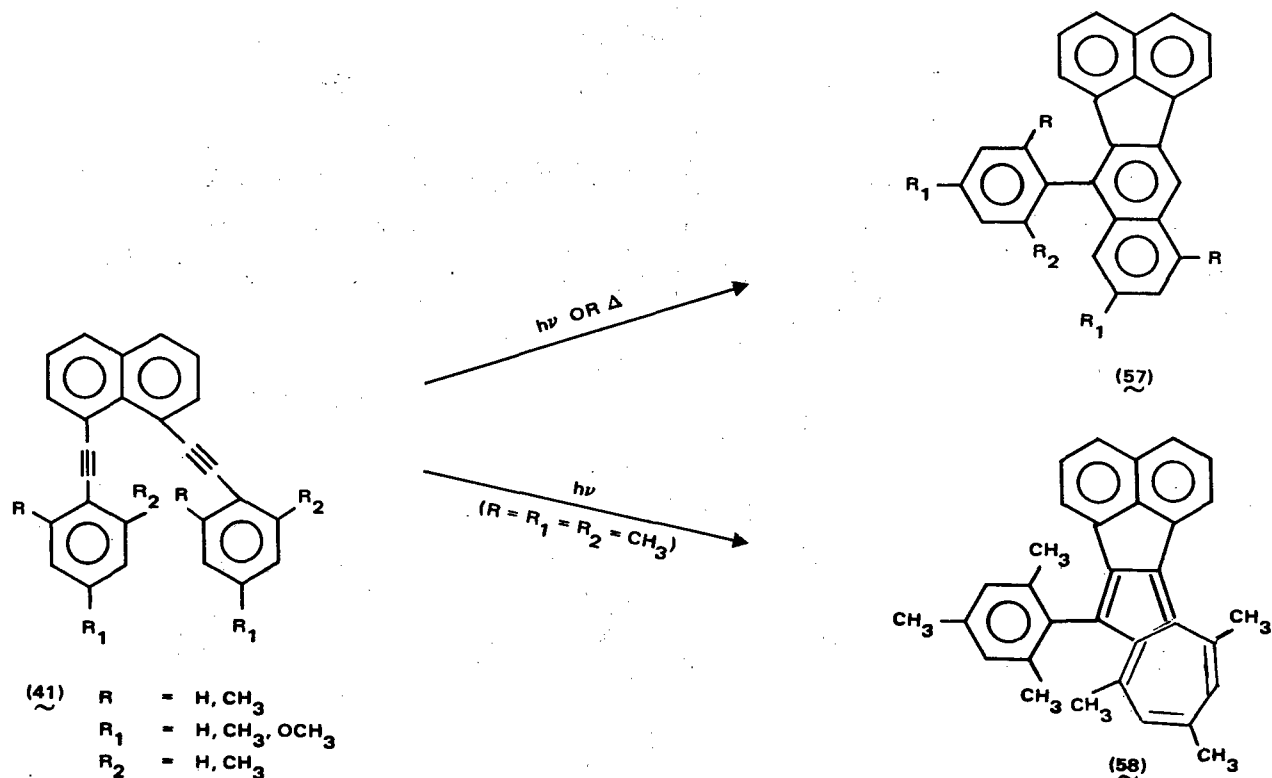
Intramolecular cyclization of $\underset{\sim}{51}$ (R = R$_1$ = R$_2$ = H) and its derivatives can be effected by heating in an inert solvent or by irradiation. The naphthalene products ($\underset{\sim}{57}$) are consistently formed. In one case (R = R$_1$ = R$_2$ = CH$_3$), the substitution pattern dictates the photochemical isomerization to the azulene derivative $\underset{\sim}{58}$, whereas its thermal reaction leads to the corresponding $\underset{\sim}{57}$, losing one methyl group in the process.

The criss-cross compound $\underset{\sim}{42}$ thermally and photochemically cyclizes to give 9-phenyl-dibenz[a,c]-anthracene ($\underset{\sim}{59}$) in good yield (References 46a and 48). The formation of highly fused aromatic structure from $\underset{\sim}{42}$ without the evolution of volatiles satisfies the most important criterion for application to thermal curing in polymer systems (vide supra: Introduction section).

(42)   **(59)**
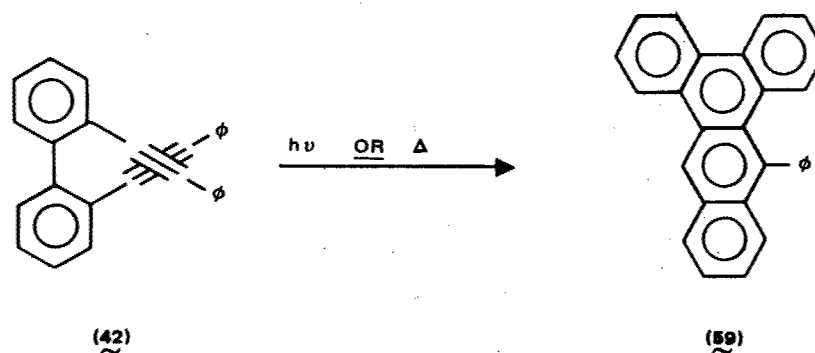
A comparative study on the organoplatinum chemistry (Reference 46a) of $\underset{\sim}{39}$, $\underset{\sim}{41}$, and $\underset{\sim}{42}$ suggests that a common reaction pathway is followed, structurally similar fused aromatic systems $\underset{\sim}{60}$-$\underset{\sim}{62}$ being formed, respectively.

(60)   **(61)**   **(62)**

34
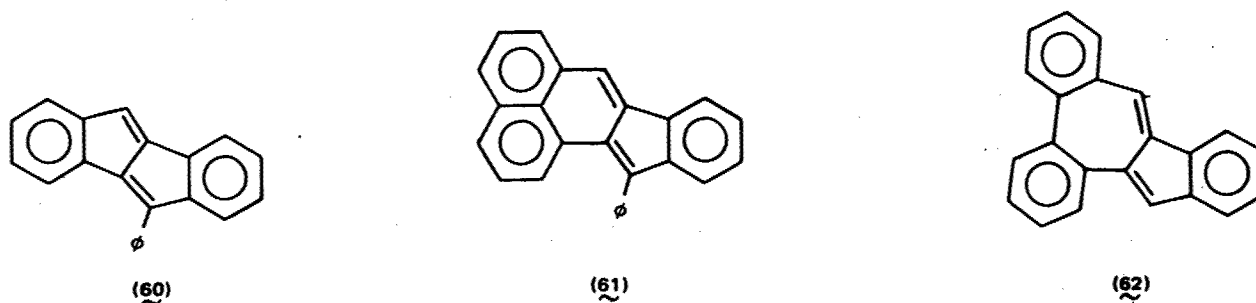
B. EVALUATION OF SELECTED SYSTEMS

Consideration of pertinent literature permits certain generalizations regarding linear organic systems which would likely undergo thermal cyclization to give highly fused aromatic and/or heteroaromatic structures. Polyenes and -ynes are promising candidates. It seems that the geometric dispositions of such unsaturated systems, e.g., cis- trans isomerism, proximity of interacting unsaturation sites, are of paramount significance. Most importantly, cyclization must be accompanied by no volatile evolution.

The systems which are currently under scrutiny for their tendency (or lack of) and modes of cyclization at elevated temperatures can be categorized according to the flow chart shown below:
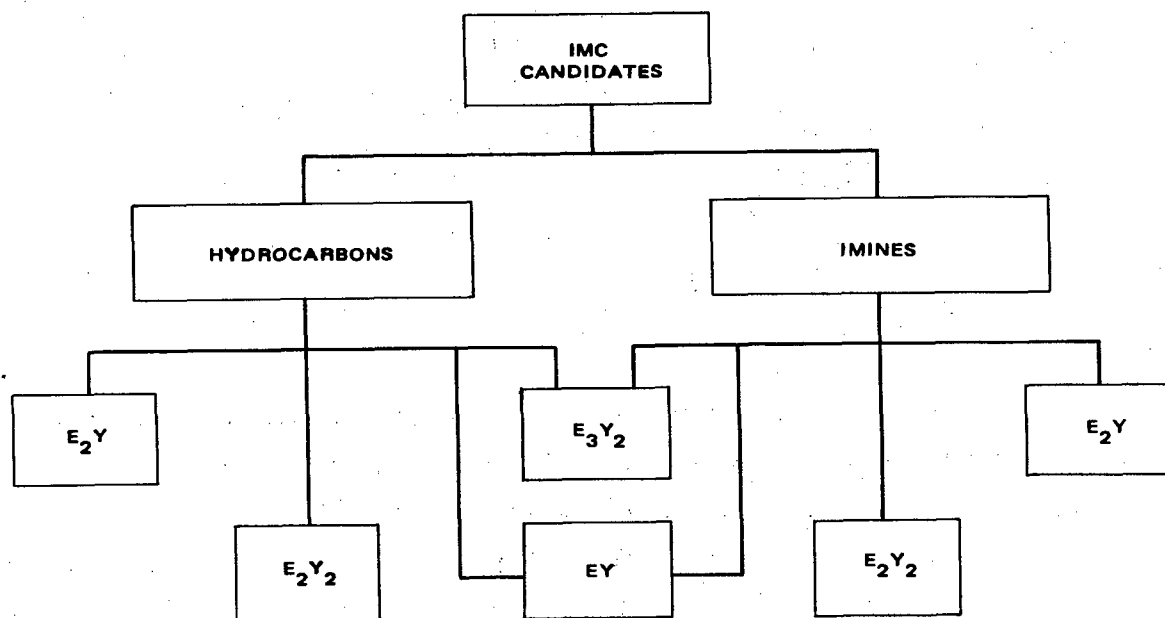
EY = enyne; E_2Y = dienynes; E_2Y_2 = diendiynes; E_3Y_2 = triendiynes

The EY Systems

The Straus and inverse-Straus coupling products have been postulated as intermediary compounds in the thermal curing of acetylene-terminating quinoxalines. Some systems containing the Straus and

35

inverse-Straus skeletons (63) are currently under investigation and will be the subject of separate technical reports.
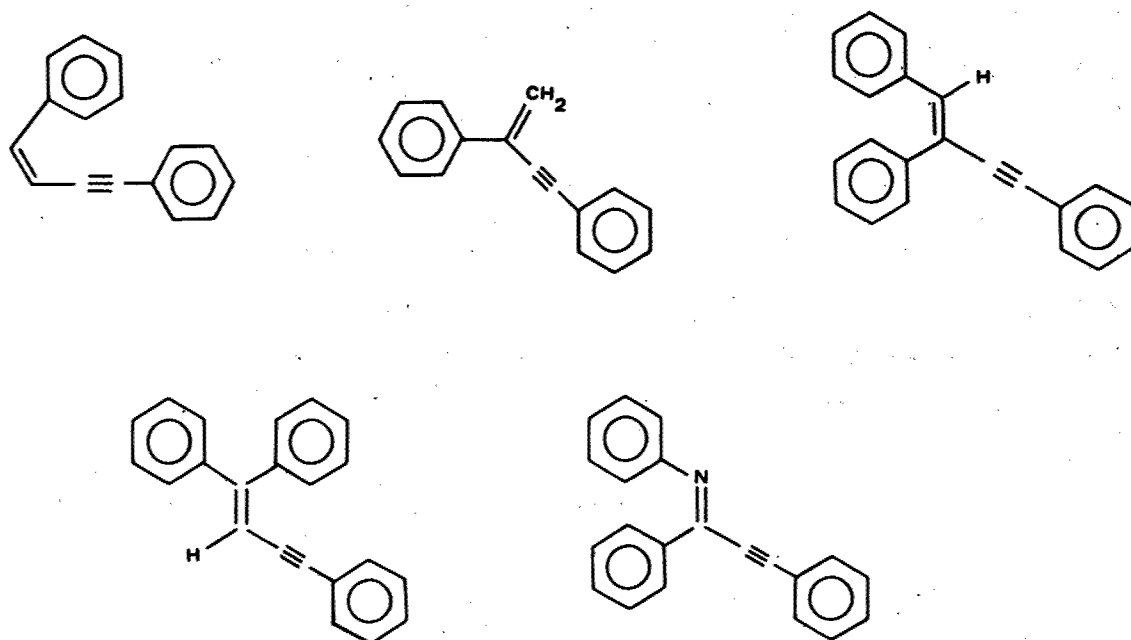
The E$_2$Y Systems

The dienyne moiety can conceivably be incorporated in polymer chains to contribute to their flexibility and thus better processability (e. g. , lowering of Tg). The dangling effect of the branching group also enhances the entropy factor. Thermal treatment of the dienynes was expected to give terphenyl structures. Interestingly, both monomeric dienynes 64a and 64b could cyclize to the same terphenyl. Different modes of difunctionalization on the terminal rings of the dienynes may lead to straight-chain or angular type catenations during polymerization.

The syntheses of monomeric 64a and 64b employ the Wittig olefination as the key step. The acetylenic ketone 64 was successfully prepared by a palladium-catalyzed reaction between benzoyl chloride and phenylacetylene (Reference 49). The phosphonium salts necessary for the Wittig synthesis were prepared by a conventional method. The phosphonium salt 66 could be

(64a)

Δ

64b

Δ

(64a) – POLYMER

φ

STRAIGHT-CHAIN

ANGULAR

φ

φ

φ

(64b) – POLYMER
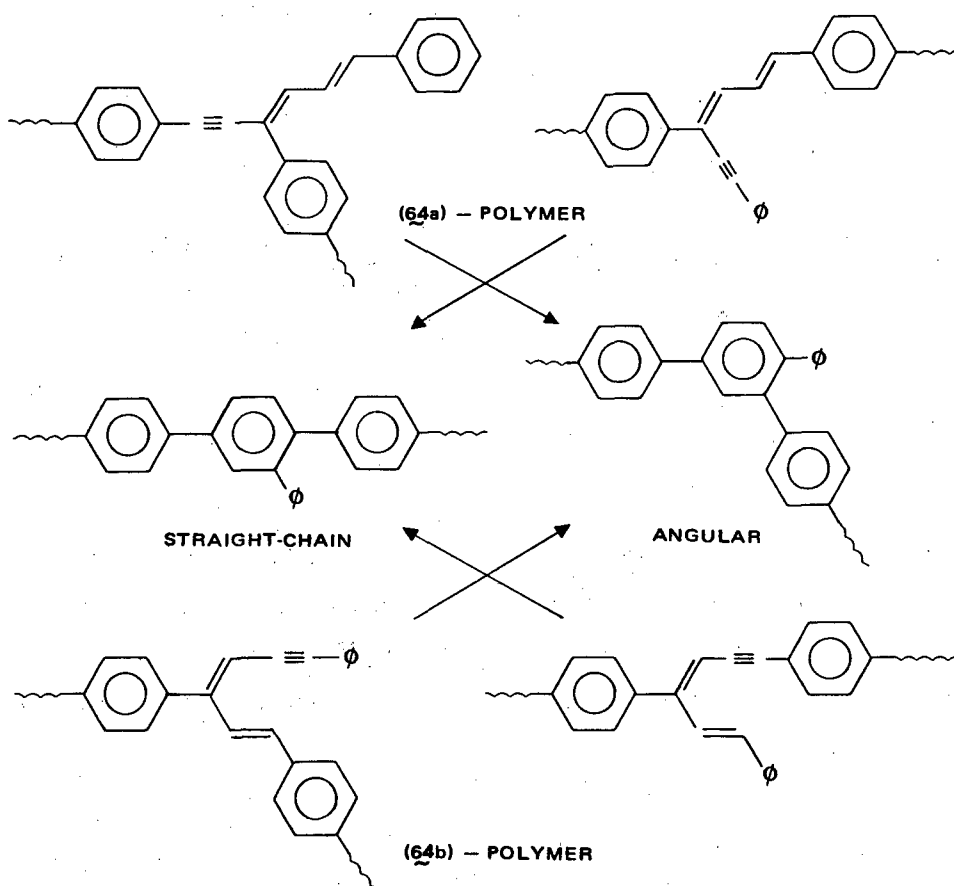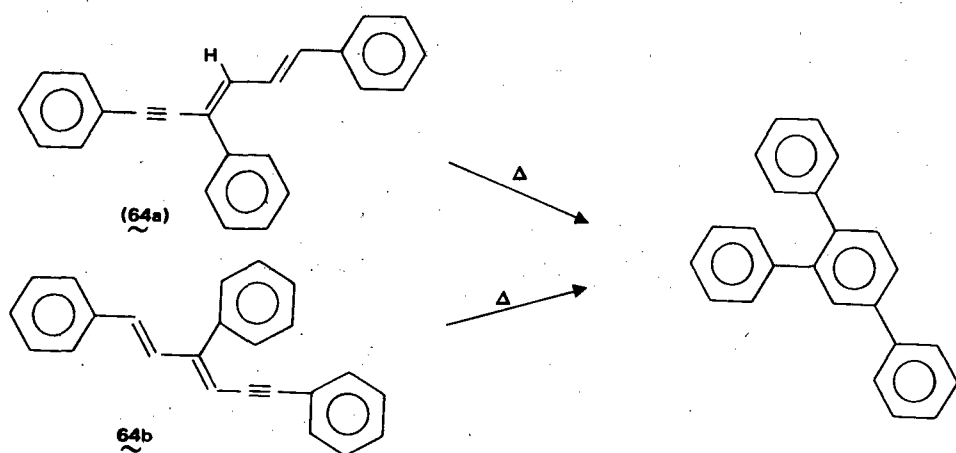
replaced by its corresponding phosphonate (Reference 50) in the Wittig synthesis but such modification did not seem advantageous (see Experimental). The phosphonium salt 67 was prepared from phenylpropargyl bromide and triphenylphosphine. The allenic structure was ascertained by infrared spectroscopy.

The propargylic form was regenerated in the ylid (Reference 51) upon treatment of $\underset{\sim}{67}$ with n-butyllithium. The yields of 64a and 64b were poor.
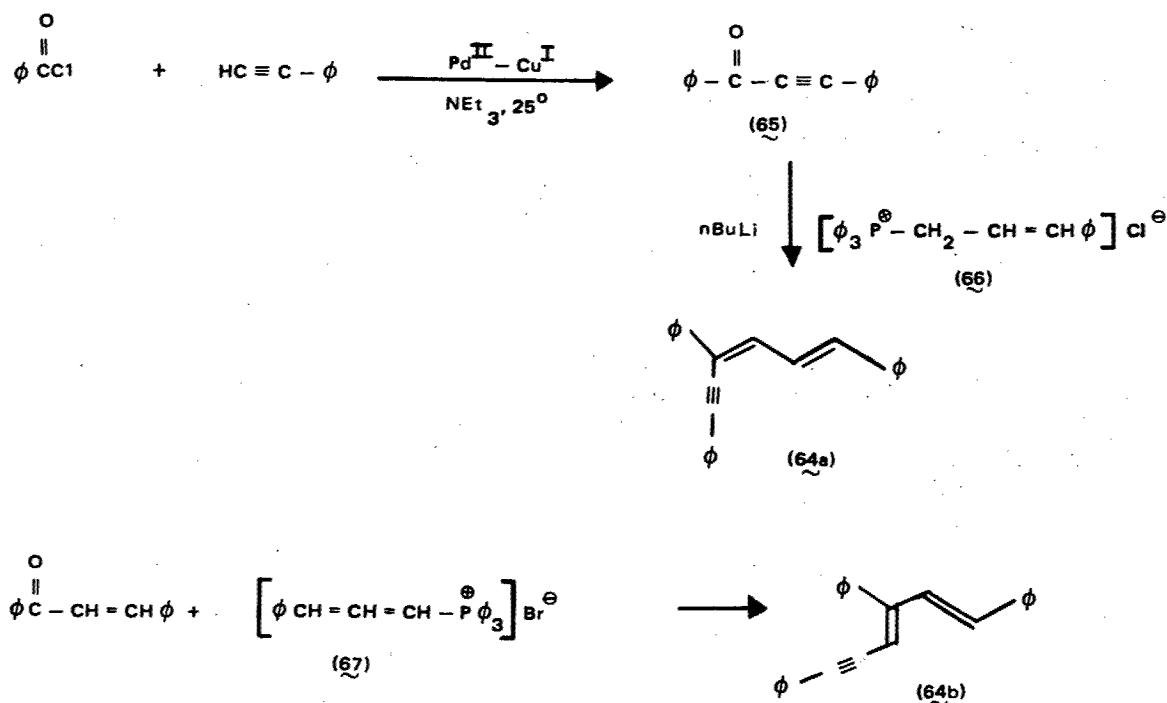
E_2Y systems having one of the double bonds as part of an aromatic ring (68) were expected to thermally cyclize into naphthalene-like structures. The <u>ortho</u> relationship of the two ends of the E_2Y system is tantamount to the <u>cis</u> configuration about a double bond. The syntheses of 68a, 68b, 68c, and 68d were undertaken.

(68a)　　　　　　(68b)　　　　　　(68c)　　　　　　(68d)
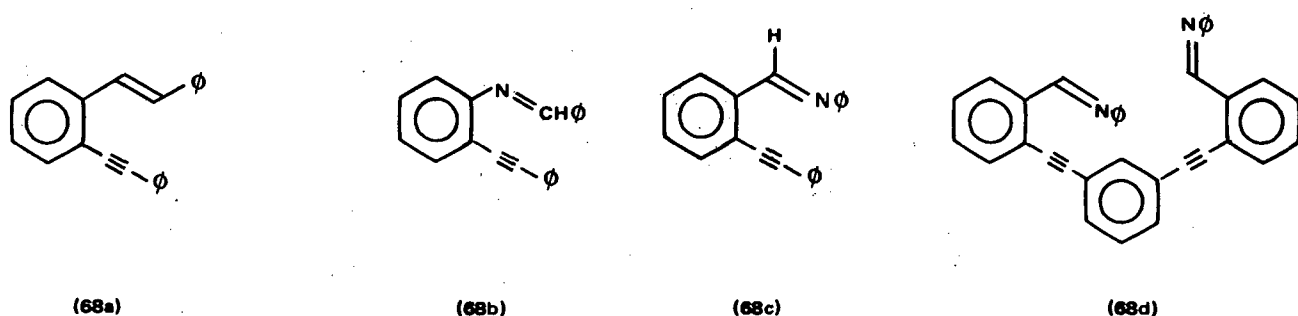
Both 68a (Reference 52) and 68c were obtained from the same aldehyde intermediate 69 (Reference 52) which was synthesized from commercially available 2-bromobenzaldehyde via a coupling reaction with phenylacetylene catalyzed by palladium [II] acetate (Reference 53).   The alternative method using the dichlorobis(triphenylphosphine)palladium [II] — copper [I] iodide catalytic system (Reference 49) was inefficient.

(69)　　　　　　(68c)
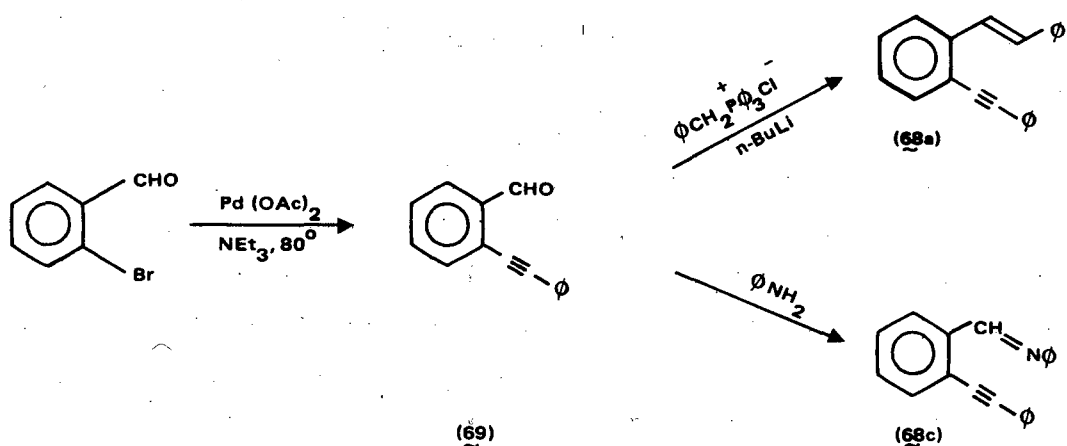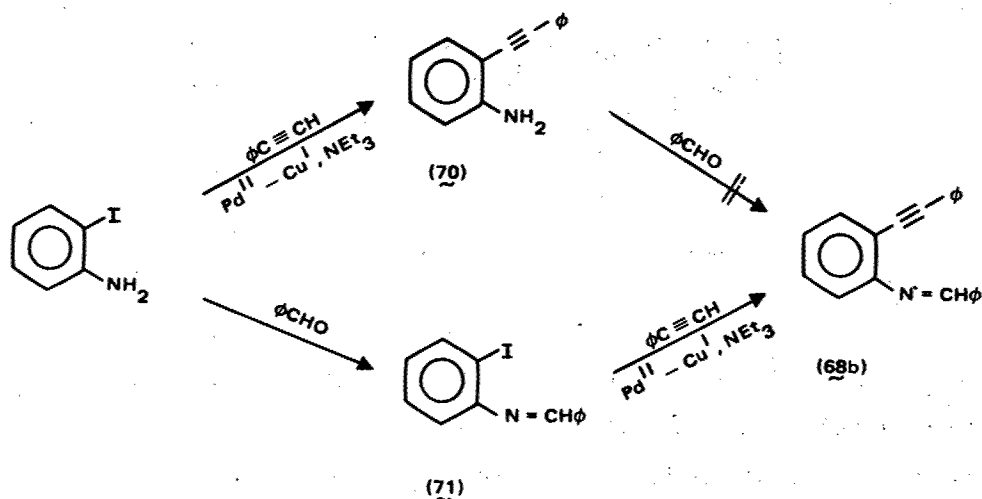
2-Aminotolane (70) is a logical precursor to the imine 68b. Unfortunately, it fails to react with benzaldehyde for reasons probably more electronic than steric, since 69 undergoes facile imine formation with aniline. The iodo-imine 71 (Reference 54) was successfully prepared from commercially available 2-iodoaniline and converted to the desired E_2Y-imine 68b. The purification of 68b was problematic owing to its instability toward silica gel, alumina and Florisil column chromatography, benzaldehyde and 2-aminotolane (70) being recovered as the products of hydrolysis of 68b. Solution to the problem was found when cellulose was used as the chromatographic material.

The availability of commercial 1,3-diethynylbenzene prompted the synthesis of the "double-barrel" analog (72) of aldehyde 69. Conversion of 72 to 68d affords a novel candidate for the intermolecular cyclization study.

(72) (68d)
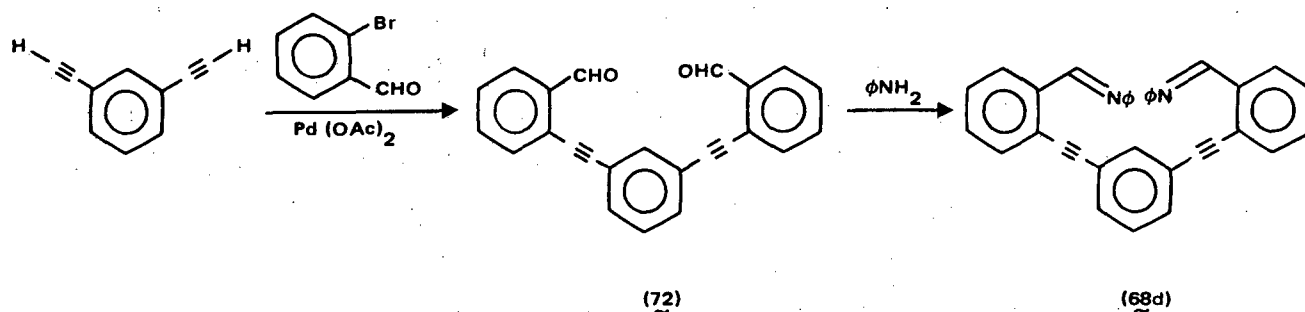
Thermal Studies on E_2Y-Systems

While the hydrocarbon E_2Y-systems 64a, 64b and 68a did not seem to undergo intramolecular cyclization reactions upon heating under nitrogen in tetralin solvent, the E_2Y-imines 68b and 68c yielded their respective <u>isomers</u> 73 and 74.*

Both 73 and 74 are higher melting than their starting materials 68b and 68c by nearly 200°. In their infrared spectra, the strong imine absorption at 1620 cm^{-1} is absent. The infrared spectrum of 73 shows a strong band at 3420 cm^{-1}, assignable to a secondary amine NH stretching frequency.

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*The condensed ring compound 73 was the sole product (23% yield) from 68b when the latter was heated at 150-160° under nitrogen in tetralin. It is interesting to note that when 68b was heated above 175° (i.e., 175-200°) in the same solvent, 73 was not formed but another crystalline white compound was obtained in 27% yield. The available physical data (ms, nmr, ir) were consistent with structure i, but structure ii could not be vigorously excluded. Raman spectroscopy may be helpful.
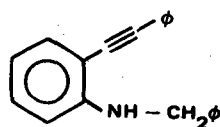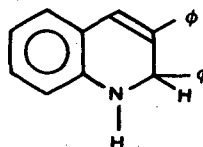
(i) (ii)

Conclusive structure proof could be obtained by independent synthesis of i from 68b by sodium borohydride reduction, and dehydrogenation of ii to the known 2,3-diphenylquinoline with DDQ.

41

The nmr spectrum of 73 indicates a singlet at δ6.10 and a broad singlet at δ8.10 corresponding to one proton each. On the basis of its high melting point, elemental analysis, infrared, nmr and mass spectra, compound 73 was assigned a structure with an indeno[1,2-b]indole skeleton. The infrared spectrum of 74 does not show a secondary amine; its high melting point and mass spectrum are consistent with a tentative structure similar to that of 73. Conclusive structure proof for 73† and 74 is in order. Dehydrogenation of 73 with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) should give the known azapentalene system 75 (Reference 55). Application of a conventional

(68b)   (73)   (75)

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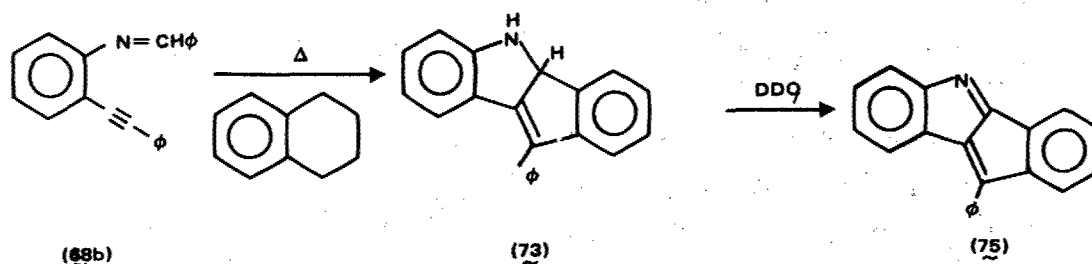
†Although the indeno [1,2-b] indole skeleton of 73 can be proved by its conversion to 75, the exact position of the double bond in the ring system cannot be vigorously established. Mechanistic intuition (least motion) would favor structure 73 but physical data are also consistent with an alternative structure 73a.

(73)   (73a)

42

(68c)   (74)   (76)
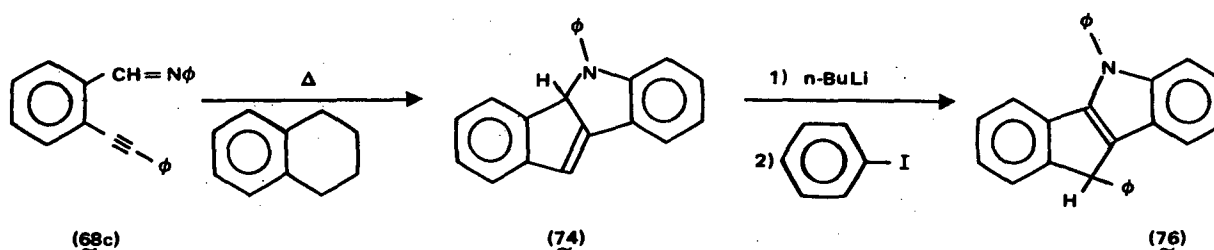
procedure in organolithium chemistry can transform 74 to another known compound 76 (Reference 55).

The thermal reaction of the "double-barrel" compound 68d was more complex, although thin-layer chromatography indicated a major component was being formed. Further work must be done to elucidate the reaction pathway. By analogy to 74, the cyclized products from 68d could be the isomeric 77a and 77b.

(77a)   (77b)
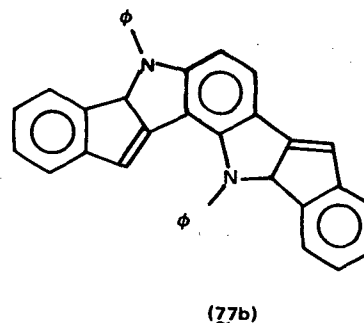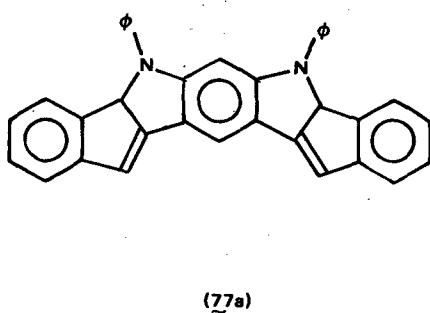
The E_2Y_2 Systems

Structurally, the biphenyl compound 42 (vide supra) is a member of the E_2Y_2 group which comprises compounds 78 having the basic skeleton of cis,cis-octa-3,5-dien-1,7-diyne.
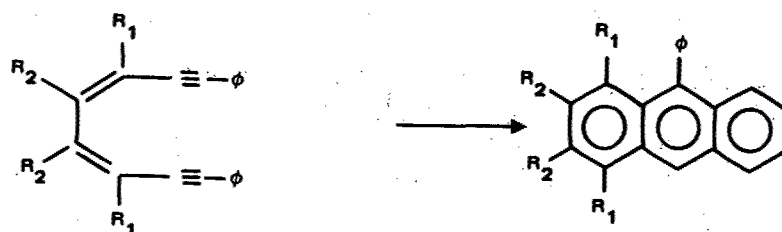
(42) $R_1R = C_4H_4$
(78a) $R_1 = R_2 = H$
(78b) $R_1 = \phi, R_2 = H$
(78c) $R_1 = H, R_2 = \phi$
(78d) $R_1 = R_2 = \phi$

(78e)

(78f)

(78g)

(78h)

(78i)
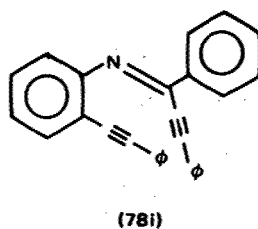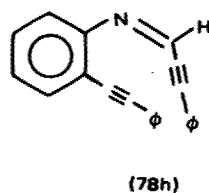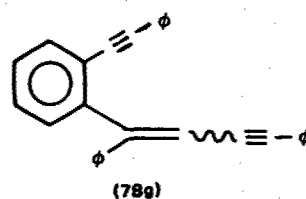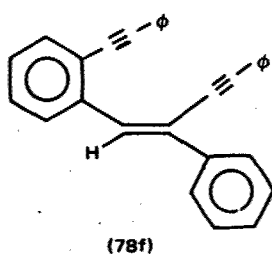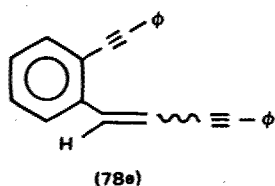
The compounds 78d, 78e, and 78f were chosen for preliminary studies. Compound 78d bears remarkable structural similarity to 42. Its incorporation into a polymer chain could add some degree of flexibility in relation to

44

(79a) X = Cl
(79b) X = Br
(79c) X = I
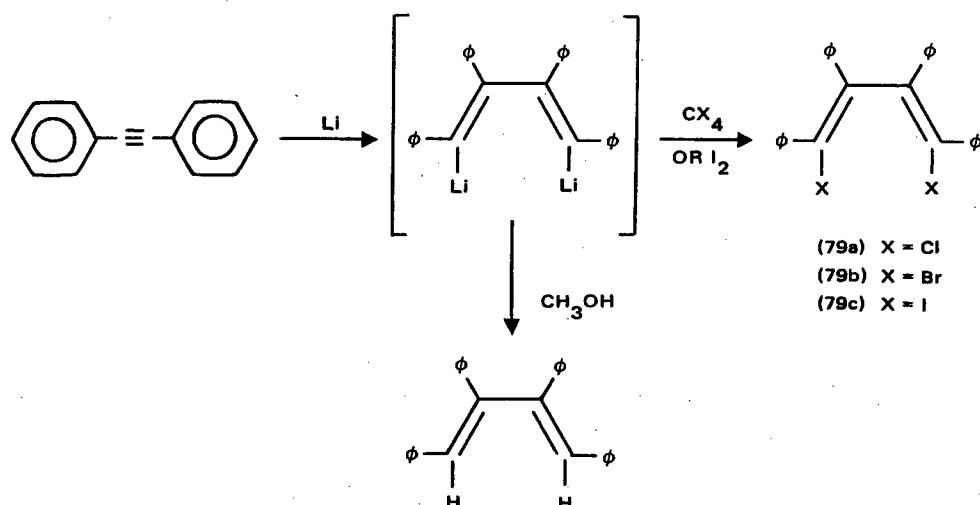
biphenylic 42. The synthetic route to 78d requires the initial preparation of 79. Treatment of diphenylacetylene with lithium wire in ether led to the formation of a yellow crystalline dilithio salt of 1,2,3,4-tetraphenylbutadiene which was dissolved in tetrahydrofuran to give a dark green solution (References 56 and 57). Quenching with carbon tetrachloride and carbon tetrabromide gave the dichloro and dibromo compounds, 79a and 79b, respectively. Treatment of the dilithio salt with iodine provided the diiodo derivative 79c (Reference 57). The cis, cis-configuration of the dilithio salt was inferred from its facile formation of various metallocycles (References 56 and 57). Several attempts in the preparation of 78d from 79 have met with failure. The difficulty was probably steric in nature.
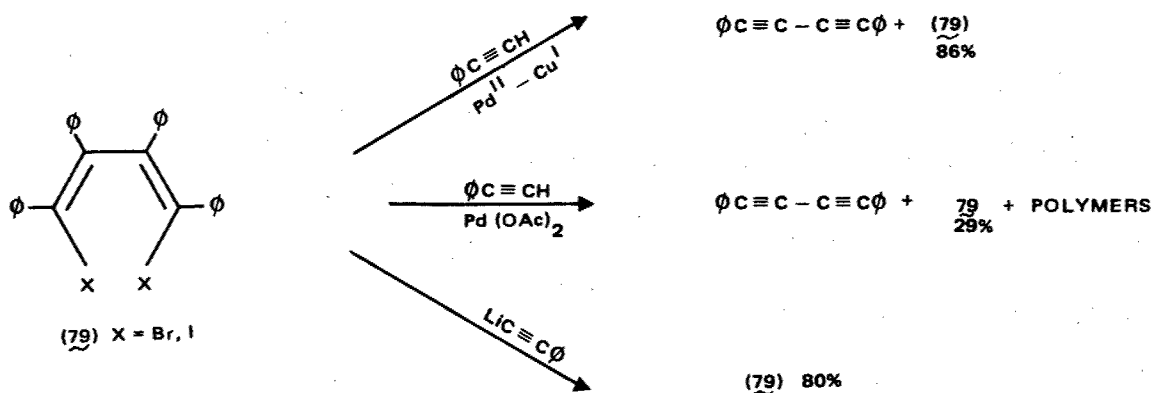
A logical alternative in this direction would be the treatment of the dilithio precursor of 79 with halogenated phenylacetylene (Reference 58).
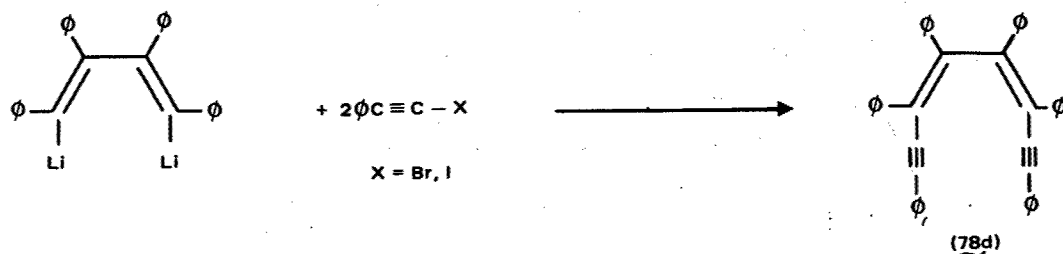
Synthesis of trans-78e was accomplished by the Wittig method. The product obtained after column chromatography was a yellow oil.

46
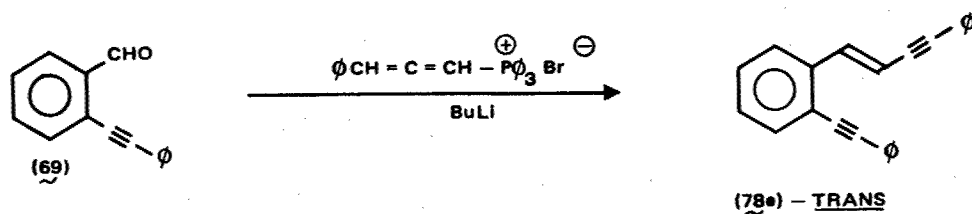
Similarly, the Wittig reaction provided a successful entry to 78f. The cis-disposition of the vinylic bromine is assumed on the basis of the relative

(78f)   (80)
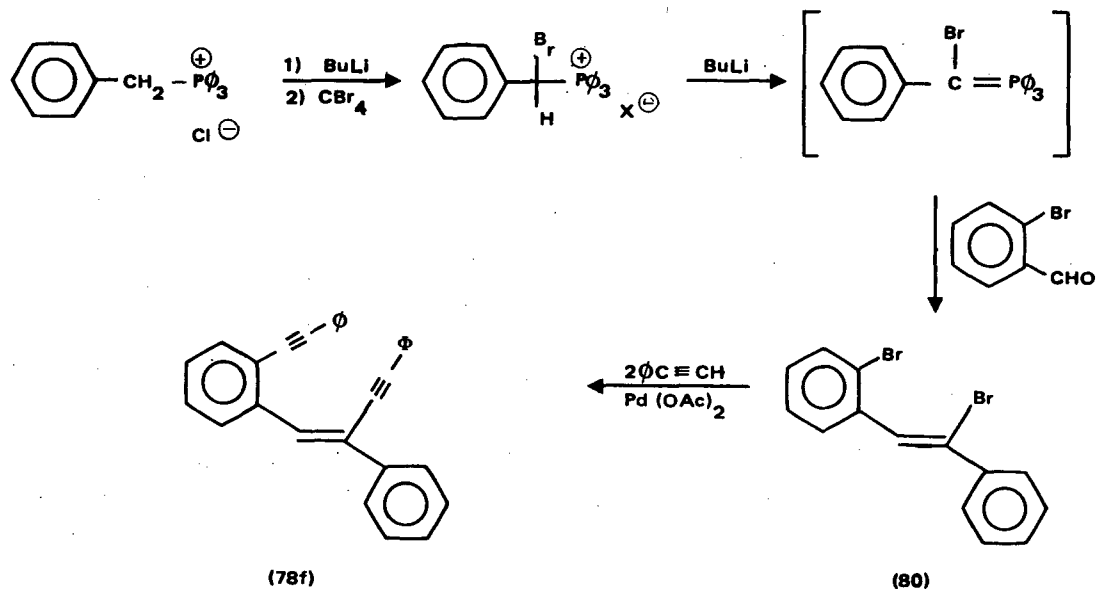
bulkiness of the bromine atom and the phenyl group.   The subsequent stereospecific reaction gave (78f) with the two phenylethynyl pendants in a cis relationship.

Thermal Studies on E_2Y_2 Systems

Compound 78e was heated in hot tetralin under nitrogen.   The recovered material after column chromatographic purification gave an infrared spectrum that was superimposable with that of authentic 78e.[*] Seemingly, the reaction condition (150-$200°$ in tetralin) chosen for the study was insufficient to cause

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[*]A 3 percent yield of a crystalline material was obtained together with recovered starting material. Infrared, mass spectrum (m/e 304) and high mp (192-$193°$) were consistent with a condensed aromatic structure, probably the product of an inefficient intramolecular cyclization.

appreciable <u>trans</u> to <u>cis</u> isomerization about the double bond so that the phenylethynyl pendants could be brought into close proximity to each other. On the other hand, when 78f was heated in tetralin at reflux for several days, no cyclization took place. The recovered material **after** purification gave a much higher melting point than 78f. The infrared spectrum showed a strong band at 900 cm^{-1} which was not present in the spectrum of 78f. Mass spectrometry established that this product was isomeric with 78f. The product was probably E-78f derivable from isomerization of the double bond via a thermally generated diradical.
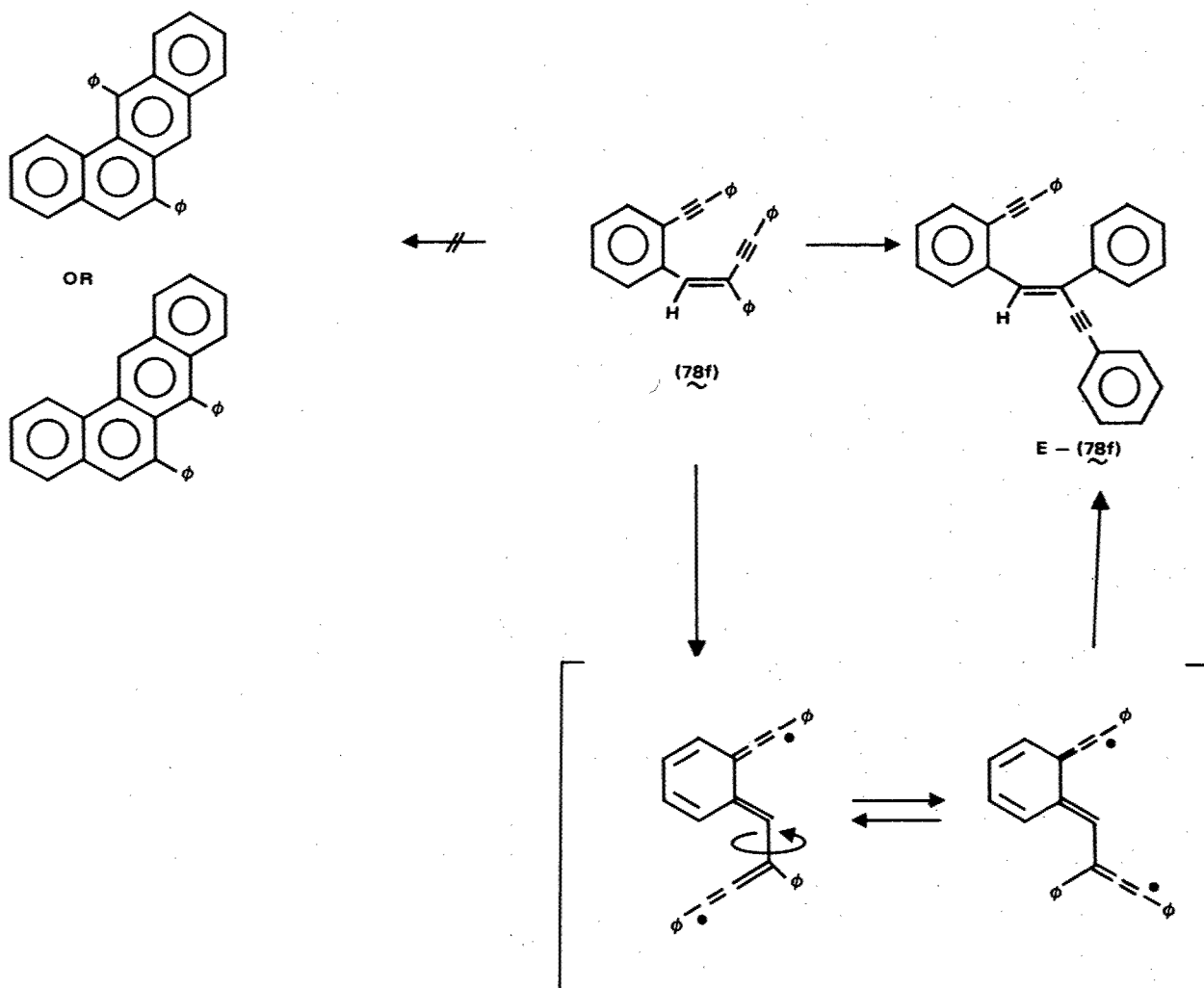
The failure of a structurally similar system (Reference 25c) to undergo thermal cyclization is probably also the result of an efficient energy wasting pathway via this diradical mechanism for cis-trans isomerization (<u>vide</u> <u>supra</u>).

The E_3Y_2 Systems

Only one compound (81) in this group has been prepared and studied. Treatment of 81 with heat did not effect intramolecular cyclization.

(81)
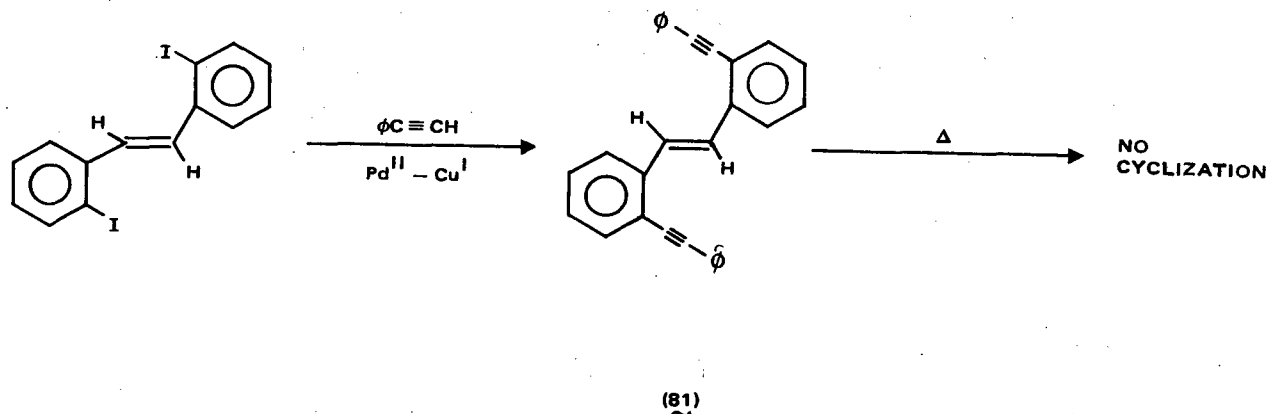
SECTION III. CONCLUSIONS AND RECOMMENDATIONS

All hydrocarbon compounds examined did not yield cyclization products. The E_2Y 64a and 64b undergo extensive polymerization under the reaction conditions. Seemingly, initial cisoid conformation of the butadiene segment is important to effect ring closure. On the other hand, the detection of cis-trans isomerization about the double bond in the E_2Y_2 system 78f casts doubt on the necessity of a cisoid arrangement of the participating units for cyclization. A low-energy thermal pathway generates the bisallenic diradical (vide supra) which then cascades down an energy-dissipating path to the trans-isomer. The successful thermal intramolecular cyclization of 42 (a member of the hydrocarbon E_2Y_2 family) probably rests in the formation of similar bisallenic diradical being deprived of the possibility of an analogous cis-trans isomerization.

50
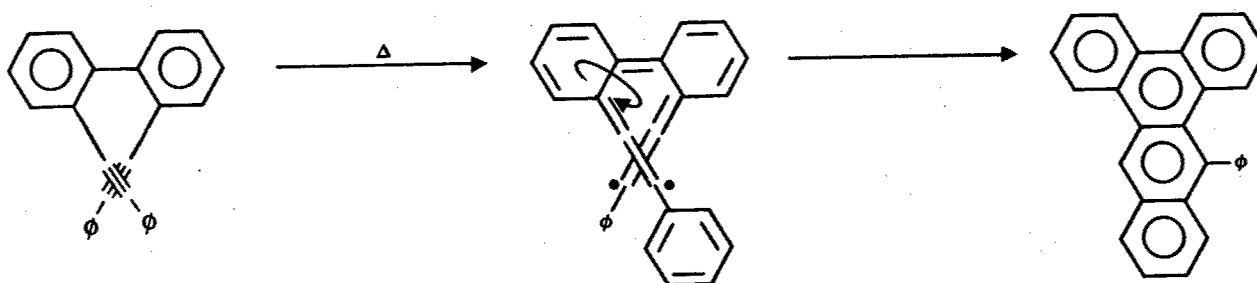
On the basis of the bisallenic diradical hypothesis, exploratory experiments with the other hydrocarbon E_2Y_2 systems 78a-c, (Z)-78e and (Z)-78g should be aborted. On the other hand, hexaphenylated system 78d would be expected to give a bisallenic diradical intermediate which must overcome a high energy barrier for cis-trans isomerization due to steric reasons. Closure of the diradical in the cisoid conformation to the fused ring skeleton thus becomes kinetically competitive.
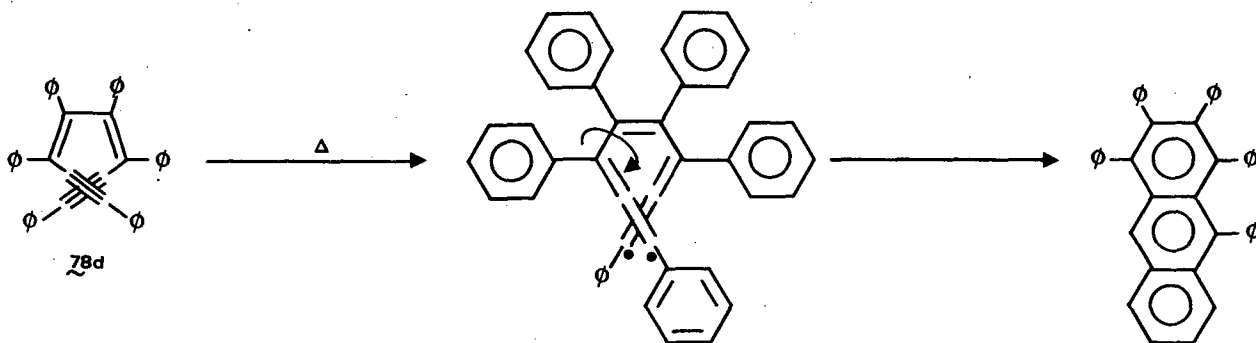
More positive results have been obtained with the imine family. The cyclized product 73 from imine 68b suggests future exploratory experiments in this direction would be promising. For example, the phenyl analog 82 of

68b   (R = H)
82   (R = φ)

73 (R = H)
83 (R = φ)

51
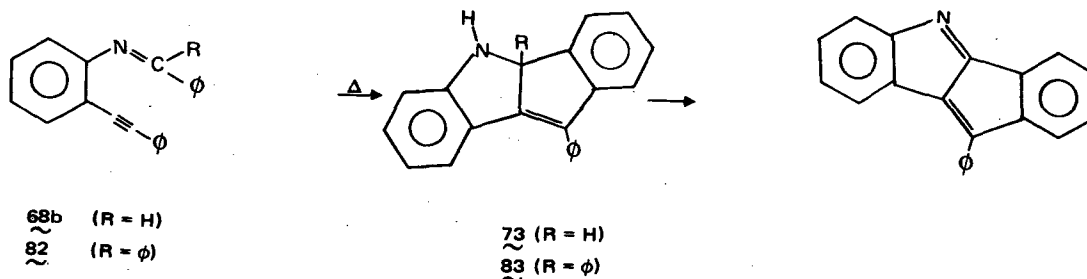
68b could be expected to give 83, which would be less likely to thermally eliminate benzene (RH) than would 73 eliminate hydrogen. Likewise, the cyclized product 74 from 68c would be rendered more thermally stable by phenylation at the bridgehead-4b position to give 84 which requires the imine precursor 85.

(68c)

74 R = H
84 R = φ

(85)
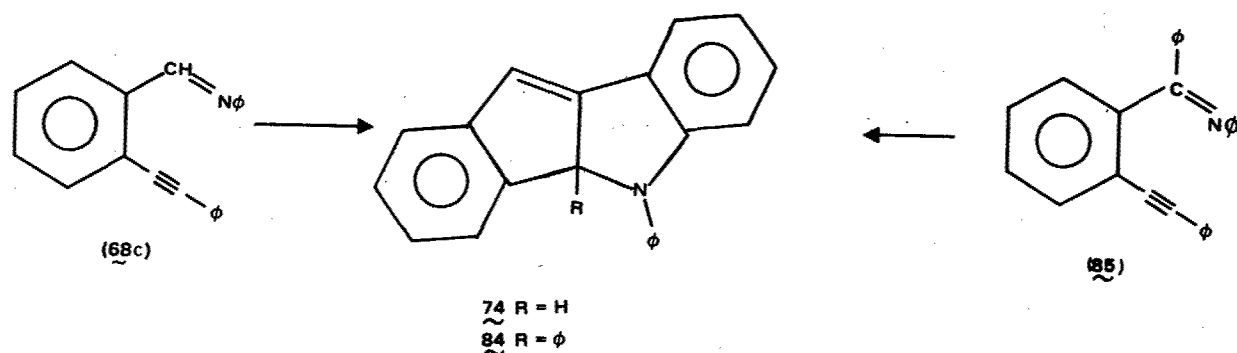
The impetus for cyclization of the imine compounds 68b and 68c can be considered as nucleophilic attack of the triple bond on the electrophilic carbon of the imine forming a stable 5-membered ring. A similar ring

(68b)

(68c)
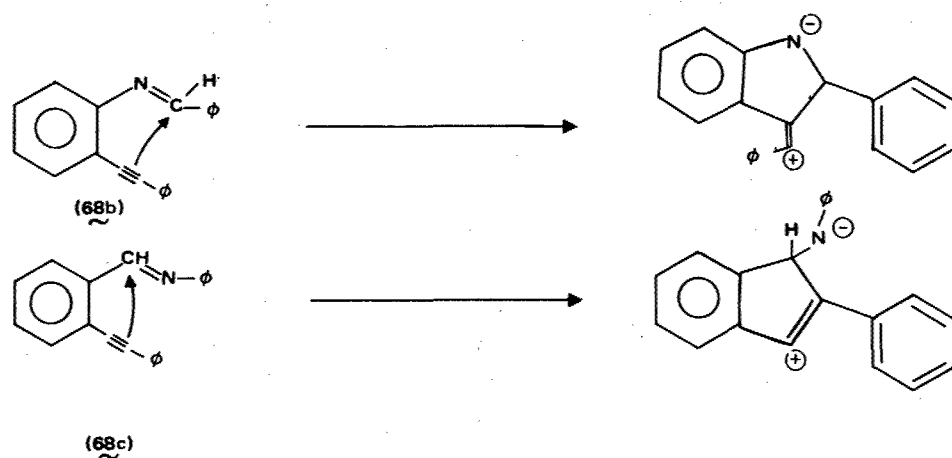
closure mechanism was invoked in the rearrangement of the quinoxaline 86 to benzimidazole (Reference 59).
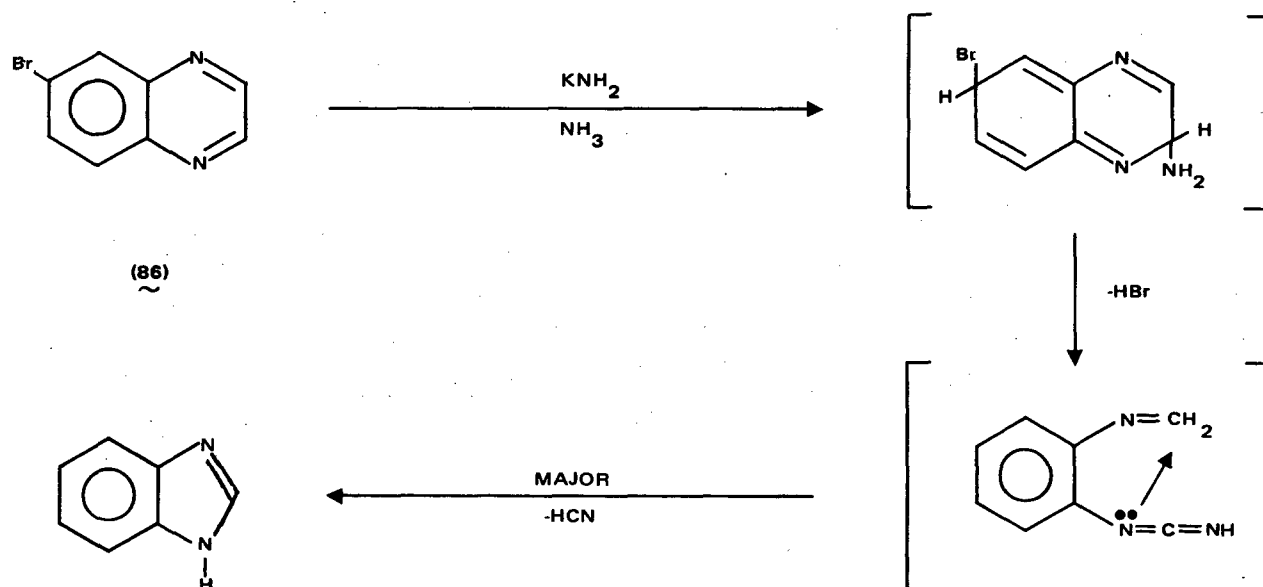
An allenic diradical mechanism is a possible alternative.
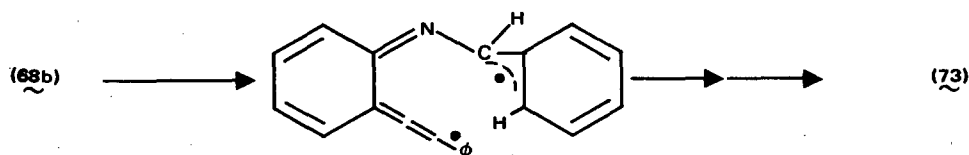
Other systems that could be under consideration as candidates for thermal intramolecular cyclization are listed below with their respective logical precursors and expected cyclization products ($78i = E_2Y_2$; $88 = E_2Y$; $89 = E_3Y_2$).

53
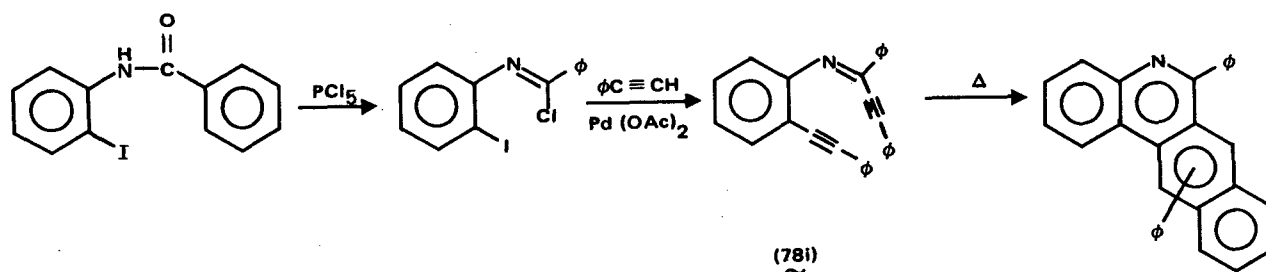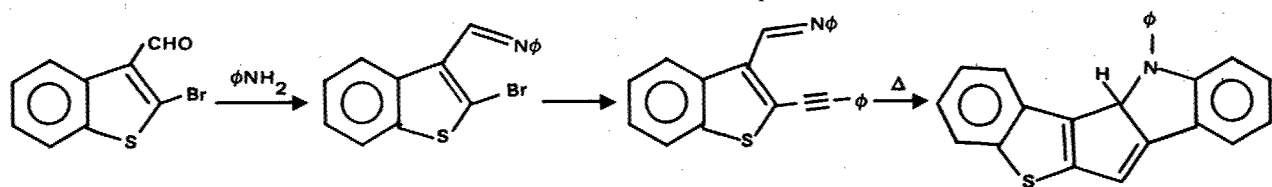
(88)
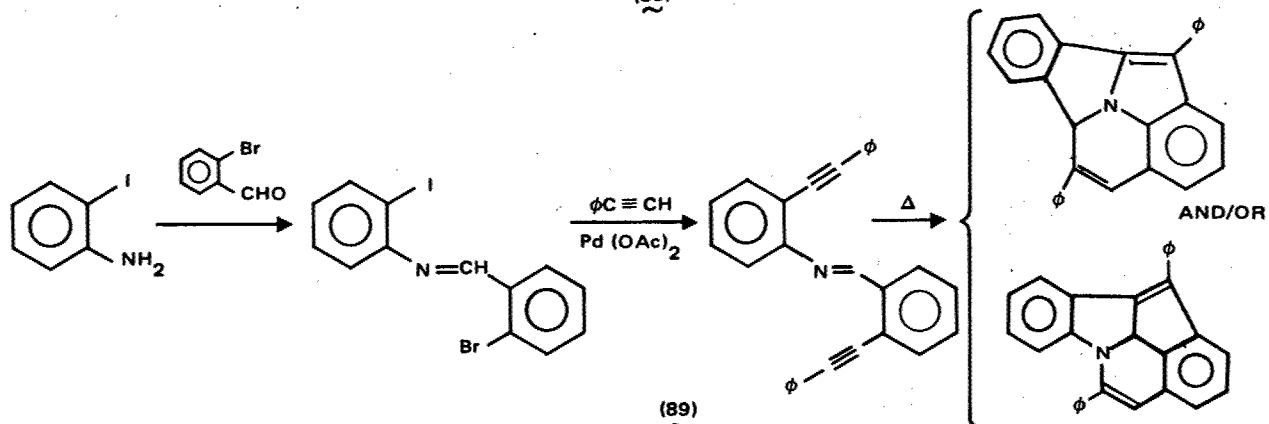
(89)

Finally, the availability of synthetic methods for the construction of 2,2'-bipyrroles (Reference 61) should make 90 an attractive candidate for thermal intramolecular cyclization reactions. The interesting possibility of a dual cyclization pathway for 90 is evident.
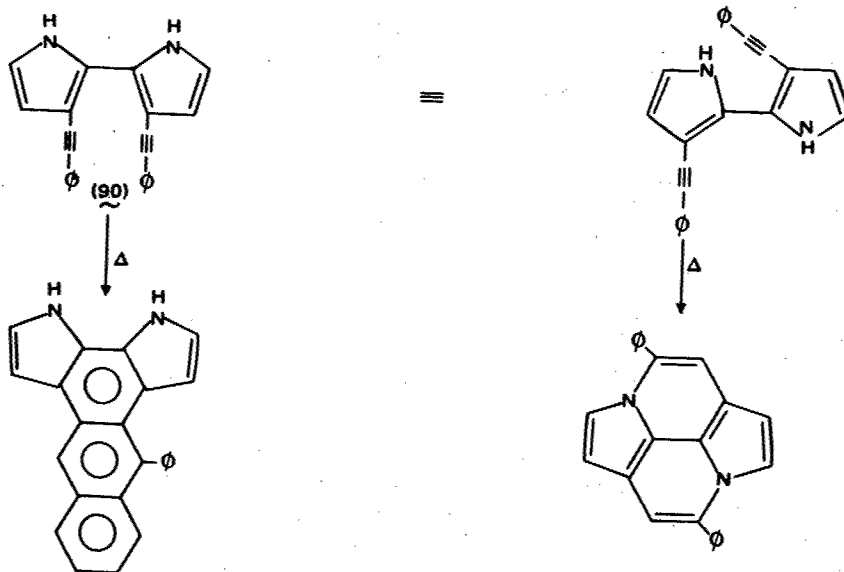
SECTION IV. EXPERIMENTAL

Synthesis of 1,4-Diphenyl-3-yn-2-one: (Reference 49)

To a deaerated 225-ml triethylamine solution of 10.20g (100.0 mmoles) of phenylacetylene (bp 139-140°) and 14.05g (100.0 mmoles) of benzoyl chloride (bp 30-31°/0.04 mmHg) were added 86.8 mg (0.124 mmole) of dichlorobis(triphenylphosphine) palladium[II] and 104 mg (0.546 mmoles) of copper[I] iodide. After stirring under nitrogen for 15 minutes the initially yellow solution deposited a copious white precipitate with concomitant generation of heat. The mixture was stirred for a total of 22 hours at 25°.

The mixture was mixed with 200 ml of chloroform and 200 ml of water. The organic phase was separated and aqueous phase extracted with 2X 100 ml of chloroform. The combined organic fractions were dried over magnesium sulfate and concentrated. Thin layer chromatography (SiO_2, 1:1 $CHCl_3$/hexane) revealed the presence of two components.

Column chromatography (SiO_2) separated 1,4-diphenyl-1,3-diyne in the hexane fraction: 200 mg; mp 86°. Continued elution with 20% chloroform-hexane and recrystallization from hexane yielded creamy-yellow crystals of 1,4-diphenyl-3-yn-2-one: 17.12g (83.11 mmoles, 83.1%); mp. 47-48° (lit.:49-50°); ir (KBr) 2200 (sharp, -C≡C-), 1630 cm^{-1} (sharp, C=O); mass spectrum: m/e 206 (M+).

Synthesis of Diethyl 3-Phenyl-2-propenylphosphonate: (Reference 50b)

A mixture of 15.26g (100.0 mmoles) of cinnamyl chloride and 17.53g (106.0 mmoles) of triethyl phosphite was heated at 180-190° under nitrogen for 17 hours. Careful distillation (126-129°/0.2 mm Hg) yielded diethyl 3-phenyl-2-propenylphosphonate: 12.92g (50.9 mmoles, 50.9%) ir (film) 1245 (strong, P=O), 1010-1050 (broad, P-O-C), 1160 (sharp, P-OCH$_2$CH$_3$), 960

55

(strong) and 745 cm^{-1}; nmr (CDCℓ_3) δ1.3 (t, 6H, C$\underline{H}_3$, J = 7.0 Hz), 2.7 (d x d, 2H, P-C$\underline{H}_2$, J_{P-C-H} = 22 Hz, J_{AB} = 7.0 Hz), 4.1 (q x q, 4H, - OC$\underline{H}_2$, J_1 = 7.0 Hz, J_2 = 7.0 Hz), 6.0 - 6.7 (m, 2H, vinyl) and 7.3 ppm (m, 5H, aromatic); mass spectrum: m/e 254 (M^{+}), 225, 117.

Synthesis of 3-Phenyl-2-propenyltriphenylphosphonium Chloride:

A mixture of 15.26g (100.0 mmoles) of cinnamyl chloride and 26.50g (101.0 mmoles) of triphenylphosphine in 100 ml toluene was heated at reflux under nitrogen for 22 hours. The white crystalline precipitate was isolated by filtration, washing with hexane and air drying: yield 16.7g (40.3 mmoles, 40.3%); mp. 224-225°.

Synthesis of 3-Phenyl-1,2-propadienyltriphenylphosphonium Bromide:
(Reference 51)

A mixture of 10.44g (53.51 mmoles) of 3-phenylpropargyl bromide and 18.26g (69.61 mmoles) of triphenylphosphine in 150 ml of toluene was heated at reflux under nitrogen for 4 hours. The mixture was then cooled and the precipitate collected and air dried for 18 hours: yield, 16.91g (37.00 mmoles, 70.0%); mp. 192-193°; ir (KBr) 1930 (intense, allene), 1440(s), 1110 cm^{-1}(s).

Synthesis of cis, trans-1,3,6-triphenyl-3,5-dien-1-yne:
Method 1 (Reference 50a):

A 25-ml benzene solution of 2.55g (10.0 mmoles) of diethyl 3-phenyl-2-propenylphosphonate and 2.00g (9.71 mmoles) of 1,4-diphenyl-3-yn-2-one was added to a two-phase system of 25 ml benzene and 25 ml 25% sodium hydroxide. After the addition of 0.30g of tetraethylammonium iodide the mixture was heated at reflux for 16 hours.

The mixture was diluted with 100 ml of water and 100 ml of chloroform. The aqueous phase was extracted with 3 X 50 ml of chloroform. The combined organic fractions were washed, dried over magnesium sulfate, and concentrated. Thin-layer chromatography (SiO$_2$, 1:1 CHCl$_3$-hexane) revealed the presence of one fluorescent product.

Column chromatography (SiO$_2$, 10% CHCl$_3$ in hexane) yielded a white solid which partially polymerized during the recrystallization process with warm hexane: yield 143 mg (5.0%), mp 95-96°; ir (KBr) 1595 (m, sharp), 1470 (m, sh), 900(s), 830 cm^{-1}(s); mass spectrum: m/e 306 (M†), 207 (M-C≡C-Ph)†.

Method 2:

The addition of 5.4 ml of a 1.93-M hexane solution of n-butyllithium (10.4 mmoles) to a 50-ml ethereal suspension of 3-phenyl-2-propenyltriphenyl-phosphonium chloride at 0° under nitrogen caused the development of an intense orange-red color. After stirring for 30 minutes at 25°, the mixture was cooled to 0° and treated with a 25-ml ethereal solution of 2.05g (9.95 mmoles) of 1,4-diphenyl-3-yn-1-one. The mixture was stirred at 25° for 18 hours, treated with 5 ml of ethanol, taken up in methylene chloride and concentrated to an orange-red mass. Thin-layer chromatography (SiO$_2$, 1:1 CH$_2$Cl$_2$-hexane) revealed the presence of one fluorescent product.

Column chromatography (SiO$_2$, 10% CH$_2$Cl$_2$ in hexane) yielded 529 mg (17.4%) of 1,3,6-triphenyl-3,5-dien-1-yne: mp. 95-96°; ir (KBr) identical with the one obtained above; mass spectrum: m/e 306 (M†).

Synthesis of 2-phenylethynylbenzaldehyde: (References 52 and 53)

A mixture of 3.70g (20.0 mmoles) of 2-bromobenzaldehyde and 2.55g (25.0 mmoles) of phenylacetylene in 50 ml of deaerated, anhydrous triethyla-mine was stirred at 25° under nitrogen as 58.2 mg (0.259 mmole) of palla-dium[II] acetate and 121.6 mg (0.464 mmole) of triphenylphosphine were added. The mixture was clear yellow. Upon heating slowly to 80° (over 45 minutes), the color of the medium turned orange and a copious white pre-cipitate was formed. The mixture was heated at 80° for an additional hour.

The cooled mixture was mixed with an equal volume of hexane filtered, and washed thoroughly with hexane. The yield of triethylamine hydrobromide was 3.59g (19.7 mmoles, 98.6%). Thin-layer chromatography (SiO$_2$, 1:2 CH$_2$Cl$_2$-hexane) revealed the presence of 1,4-diphenyl-1,3-diyne and a fluor-escent product.

Column chromatography (SiO_2) separated the Glaser product (white needles, mp 85°) in the hexane eluate. Elution with 20% CH_2Cl_2 in hexane followed by recrystallization from hexane at -78° yielded 2-phenylethnylbenz-aldehyde: 3.60g (17.5 mmoles, 87.4%); ir (KBr) 2840-2740 (sharp, - C<u>H</u>O), 2220 (sharp, -C≡C-), 1690 cm^{-1} (broad, carbonyl): **mass spectrum: m/e** 206 (M$^+$); nmr ($CDCl_3$) δ7.2-7.6 (m, 8H, aromatic) 7.9 (m, 1H, ortho H on ring) and 10.6 ppm (s, 1H, CHO).

Owing to its mp being around 25°, analytically pure product could not be obtained by crystallization. Spectral evidence (and tlc homogeneity) supported the correct structure.

The alternative metal catalyst system used to effect coupling between 2-bromobenzaldehyde and phenylacetylene was dichlorobis(triphenylphos-phine) palladium[II], copper[I] iodide in triethylamine (Reference 49). The reaction was incomplete after 17 hours at 65°. The method was considered inferior to the Heck procedure (Reference 53).

Synthesis of trans-(2-Phenylethynyl)stilbene (Reference 52):

The Wittig reagent was prepared by treatment of 9.99g (25.7 mmoles) of benzyltriphenylphosphonium chloride in anhydrous ether with 29.5 ml of a 0.96-M hexane solution of n-butyllithium under nitrogen at 0°. The orange-colored ylide was stirred at 25° for 1 hour and treated with 5.23g (25.4 mmoles) of 2-phenylethynylbenzaldehyde. The resulting mixture was stirred at 25° for 16 hours.

The mixture was diluted with 130 ml of hexane and was filtered. The filtrate was concentrated and was shown by thin-layer chromatography (SiO_2, 1:2 CH_2Cl_2-hexane) to contain a fluorescent product as the only component. Purification by column chromatography on silica gel eluting with hexane yielded 831 mg (3 mmoles, 12%) of crystalline product: mp 94-94.5°; ir (KBr) 2200 (weak, sharp) 1590 (m, sh), 1490 (strong), 965 cm^{-1} (strong); mass spectrum: m/e 280 M$^+$).

Synthesis of N-(2-Phenylethynyl)benzylidene-aniline:

Upon mixing of 2.42g (11.8 mmoles) of 2-phenylethynylbenzaldehyde and 1.10g (11.8 mmoles) of distilled aniline a yellow precipitate formed

instantaneously with slight heat formation. The mixture was treated with 75 ml of petroleum ether and 0.5g of magnesium sulfate and was heated at reflux for 15 minutes. Filtered while hot, the yellow solution was evaporated down to half of the original volume, cooled to 25° and then chilled at -78°.

The white solid was isolated by filtration, redissolved in hexane, treated with charcoal and recrystallized. The purified product weighed 2.48g (74.7%); mp $63-64^{O}$; ir (KBr) 2200 (weak), 1620 (sharp, medium, C=N), 1580, 1490 cm^{-1}; mass spectrum: m/e 281 (M+), 204, 104; nmr (CDCl$_3$) δ7.2-7.6 (m, 13H, aromatic), 8.3 (M, 1H, ortho H on ring), and 9.1 ppm (S, 1H = CH).

Anal. Calc. for C$_{21}$H$_{15}$N (281.358): C, 89.65   H, 5.37   N, 4.98

Found: C, 89.28   H, 5.14   N, 5.14

NOTE: A second experiment using 36-mmoles quantities of reactants gave a 70-percent yield of product.

Synthesis of N-Benzylidene-2-iodoaniline (Reference 54):

A mixture of 21.9g (100 mmoles) of iodoaniline and 10.6g (100 mmoles) of benzaldehyde was heated without a solvent at ca. 80° for 3.5 hours. The gummy purple mixture was mixed with hot hexane and the supernatant was decanted. Upon cooling to -78°, the hexane supernatant yielded a white pre-cipitate: yield 23.6g (76.9 mmoles, 76.9%); mp $57-57.5^{O}$ (lit. 57.5^{O}); ir (KBr) 1620 (sharp, C=N), 1570 cm^{-1} (sharp, aromatic); mass spectrum: m/e 307 (M+), 180 (M-I).

Synthesis of N-Benzylidene-2-aminotolane:

A mixture of 5.652g (18.41 mmoles) of N-benzylidene-2-iodoaniline and 1.882g (18.45 mmoles) of phenylacetylene in 30 ml deaerated, anhydrous triethylamine was stirred at 25° under nitrogen as 18.0 mg of dichlorobis-(triphenylphosphine)palladium[II] and 21.8 mg of copper[I] iodide were added. After 3 hours, the mixture was filtered to remove triethylamine hydroiodide (3.907g, 92.67%). The filtrate was concentrated and pumped at 0.1 mm to

remove the last trace of triethylamine. The yellow oil was mixed with 1:5 CH_2Cl_2-hexane, treated with 1g of charcoal and filtered through Celite. Upon cooling to -78° the filtrate yielded a pale yellow crispy solid: 3.30g (11.7 mmoles, 63.8%); mp 64-65°; ir (KBr) shows the absence of NH absorptions and a strong imine band at 1625 cm^{-1}; mass spectrum: m/e 281 (M+), 204, 194, 193, 181.

The imine product was extremely sensitive hydrolytically. Attempts to purify the product by column chromatography using silica gel, Florisil (15% MgO in SiO_2), basified silica gel and neutral Woelm alumina resulted in the isolation of benzaldehyde and white needles of 2-aminotolane (mp 91-92°).

Column chromatography of the crude imine product through cellulose provided a method for purification. The pale yellow crystals obtained had mp 66-67°.

Synthesis of 1,3-diphenylethynylbenzene-2',2''-dicarboxaldehyde Anil:

A mixture of 1.00g (10.7 mmoles) of freshly distilled aniline and 1.67g (5.00 mmoles) of 1,3-diphenylethynylbenzene-2',2''-dicarboxaldehyde was heated in refluxing petroleum ether for 0.5 hour and then cooled gradually to -78°. The white crystals were isolated by filtration and washing with cold hexane: yield 2.19g (4.53 mmoles, 90.5%); mp 118-119°, ir (KBr) 1625, 1595, 1490 cm^{-1} (sharp, strong).

Thermal Intramolecular Cyclization of N-Benzylidene-2-Aminotolane. Formation of 4b,5-Dihydro-10-phenyl-indeno[1,2-b]indole:

A solution of 1.00g (3.56 mmoles) of N-benzylidene-2-aminotolane in 3.0g of deaerated tetralin was heated under nitrogen at 150-160° for 6 hours. Thin layer chromatography (SiO_2) was used to monitor the progress of the reaction. At the end of the heating period, tℓc indicated total disappearance of the starting imine and the presence of one major component:

The crude and dark brown oil was purified by column chromatography on silica gel. Elution with hexane removed tetralin. Elution with 20-50% CH_2Cl_2 in hexane yielded a white granular solid: 233 mg (23.2%); mp 264°; ir (KBr) 3420 (strong, NH), 1600 (medium) 1490, 1450 cm^{-1}; mass spectrum:

m/e 281 (M+); nmr (CDCl$_3$) δ6.1 (S, 1H, methine), 6.8-7.5 (m, 13H, aromatic) and 8.0 ppm (broad S, 1H, NH).

<u>Anal.</u> Calc. for C$_{21}$H$_{15}$N (281.359): C, 89.65 H, 5.37 N, 4.98
Found: C, 89.28 H, 5.42 N, 5.56

<u>NOTE:</u> A second experiment using 2.00g of imine in 6.0g of tetralin under the same conditions required 30 hours total heating time.

Attempted Thermal Cyclization of N-Benzylidene-2-Aminotolane in Tratralin at Above 175°. Reduction of N-Benzylidene-2-Aminotolane:

A solution of 5.499g (19.57 mmoles) of N-benzylidene-2-aminotolane in 14g deaerated tetralin was heated under nitrogen at 175° for 27 hours. The progress of the reaction was followed by thin-layer chromatography at convenient intervals. One minor and one major product were observed. (Prolonged heating — 175°, 96 hours; reflux, 70 hours — did not change the appearance of the thin-layer chromatogram).

Column chromatography (SiO$_2$) gave four fractions: Fraction 1 (hexane eluant) was recovered tetralin. Fraction 2 (10% CH$_2$Cl$_2$ in hexane) was a small amount of a yellow oil. Fraction 3 (25% CH$_2$Cl$_2$ in hexane) yielded a white crystalline solid. Fraction 4 (50% CH$_2$Cl$_2$ in hexane) gave some yellow gummy material.

The white crystalline solid was purified by recrystallization from hexane: yield 1.51g (5.36 mmoles, 27.4%); mp 102-103°; ir (KBr) 3420 (NH, strong), 1600 cm^{-1} (medium); mass spectrum: m/e 283 (M+); nmr (CDCl$_3$) δ4.24 (S, 2H), 6.82-7.80 (m, 14H, aromatic) and 8.06 ppm (broad S, 1H, NH).

Thermal Intramolecular Cyclization of N-(2-phenylethynl) benzylidene-aniline. Formation of 4b,5-Dihydro-5-phenylindeno[1,2-b]indole:

A solution of 4.00g (14.2 mmoles) of N-(2-phenylethynyl)benzylidene-aniline in 10.0g of tetralin was deaerated by bubbling nitrogen and then heated under nitrogen at 175° for 7 hours. The progress of the reaction was followed

by hourly thin-layer chromatography (SiO_2, 1:2 CH_2Cl_2-hexane). The mixture was cooled to room temperature and taken up in 100 ml of hexane. An off-white precipitate was obtained and decolorized with charcoal: yield 772 mg (2.75 mmoles, 19.3%); mp: 277-281° (dec); ir (KBr) 1590, 1490 (strong, sharp) 1240 cm^{-1} (broad, medium); mass spectrum: m/e 281 (M+).

Synthesis of 1,4-dibromo-1,2,3,4-tetraphenylbutadiene:

The lithium reagent 1,4-dilithio-1,2,3,4-tetraphenylbutadiene was prepared according to the Gilman procedure (Reference 56). The mixture of 4.42g (24.8 mmoles) of diphenylacetylene and 0.172g (24.8 mmoles) of cut lithium wire was stirred under nitrogen in 50 ml of absolute ether at room temperature. A red color developed after 30 minutes. After 15 hours, the mixture was mixed with 50 ml of tetrahydrofuran (THF) to give a green solution of the dilithio reagent.

A 2-ml aliquot of the green solution was removed and treated with 10 ml of anhydrous ethanol to give a 70% yield of 1,2,3,4-tetraphenylbutadiene: mp 183-184° (lit. 183-185°); mass spectrum: m/e 358 (M+).

The green solution was cooled to -78° when a 20-ml THF solution of 8.23g (24.8 mmoles) of carbon tetrabromide was added. The resulting mixture was stirred at room temperature for 1 hour, poured into 300 ml of water and the phases were separated. The aqueous layer was extracted with 3 X 200 ml ether. All organic fractions were combined, dried over magnesium sulfate and concentrated to a brown oil. Column chromatography (silica gel) eluting with hexane separated 0.955g of unreacted carbon tetrabromide. Elution with 10% CH_2Cl_2 in hexane yielded 4.16g (8.06 mmoles, 65.0%) of 1,4-dibromo-1,2,3,4-tetraphenylbutadiene: mp 148-148.5°; ir (KBr) 1590 (medium), 1480, 1435 cm^{-1} (strong, sharp); mass spectrum: m/e 518, 516, 514 (M+), 537, 535 (M-Br)$^{+}$.

Synthesis of 1,4-Diiodo-1,2,3,4-tetraphenylbutadiene:

Treatment of 8.90g (50.0 mmoles) of diphenylacetylene with 0.349g (50.3 mmoles) of cut lithium wire in anhydrous ether at 25° for 16 hours gave

1,2-dilithio-1,2,3,4-tetraphenylbutadiene which solubilized in THF to give a dark green solution. After cooling to -80°, the green solution was treated with a 50-ml THF solution of 10.1g (39.7 mmoles, 79.5% equivalent) of iodine. The orange yellow mixture was stirred at 25° for 2 hours, diluted with 500 ml of water and extracted with 3 X 200 ml of CH_2Cl_2. The organic fractions were combined, washed with water and dried over magnesium sulfate.

Column chromatography (silica gel) separated 1.55g of diphenylacety-lene (mp 60.5°) by elution with hexane. Elution with 20% CH_2Cl_2 in hexane yielded 5.96g (9.77 mmoles, 47.3%) of 1,4-diiodo-1,2,3,4-tetraphenylbuta-diene: mp 197.5° (decomposed); ir (KBr) 1590, 1570 (weak) 1490, 1480, 1435 cm^{-1} (strong, sharp).

Attempted Reaction Between 1,4-Dibromo-1,2,3,4-tetraphenylbutadiene and Lithium Acetylide:

A suspension of lithium acetylide in anhydrous benzene was prepared by treatment under nitrogen of 0.456g (4.47 mmoles) of phenylacetylene with 2.6 ml of a 1.8M-hexane solution of n-butyllithium. The white suspension was stirred at 25° for 30 minutes and then treated with 1.09g (2.11 mmoles) of 1,4-dibromo-1,2,3,4-tetraphenylbutadiene in benzene. The mixture was stirred at reflux for 20 hours, cooled and poured into 100 ml of water. Extraction of the reaction mixture with 100 ml CH_2Cl_2, drying and concen-tration of the organic extract yielded a yellow solid. Thin-layer chroma-tography (SiO$_2$, 1:3 CH_2Cl_2-hexane) showed only one component.

Column chromatography (silica gel) eluting with 10% CH_2Cl_2-hexane yielded a white solid which was identified as the starting dibromo compound: recovery 867 mg (79.7%); mp 147-148°, ir (KBr) superimposable with that of starting material.

Attempted Coupling Reactions Between 1,4-Dibromo-1,2,3,4-tetraphenyl-butadiene and Phenylacetylene:

Method 1

A mixture of 1.033g (2.002 mmoles) of 1,4-dibromo-1,2,3,4-tetra-phenylbutadiene and 0.4153g (4.072 mmoles) of phenylacetylene in 30 ml of

a deaerated 1:1 triethylamine-benzene solvent system was stirred under nitrogen while 14.4 mg of dichlorobis(triphenylphosphine)palladium[II] and 17.1 mg of copper[I] iodide were introduced. The initial yellow color of the mixture turned dark brown. After stirring at 25° for 8 hours, the mixture was quenched with water. The phases were separated and the organic phase was diluted with 100 ml of CH_2Cl_2, extracted with 2 X 100 ml of water and dried over magnesium sulfate. Filtering and concentrating of the filtrate gave a brown oil which was shown by thin-layer chromatography (SiO_2, 1:2 CH_2Cl_2 in hexane) to contain two components. Eluting the crude material through a silica gel column separated the Glaser diyne product in the hexane fraction and a white solid in the 5% CH_2Cl_2-in-hexane fraction. The white solid had mp 147-148° and an ir spectrum superimposable with that of 1,4-dibromo-1,2,3,4-tetraphenylbutadiene: recovery 885 mg (85.7%).

Method 2

Treatment of the dibromo compound and phenylacetylene with palladium[II] acetate and triphenylphosphine in triethylamine at 100° for 2 hours led to the isolation of the Glaser diyne product and a 28.5% recovery of starting material (mp 147-148°) by column chromatography.

Attempted Coupling Reaction Between 1,4-Diiodo-1,2,3,4-tetraphenylbutadiene and Phenylacetylene:

Parallel experiments described above were carried out with 1,4-diiodo-1,2,3,4-tetraphenylbutadiene. No coupling reaction product was isolated.

Synthesis of trans-(2'-Phenylethynyl)-1,4,-diphenyl-1-en-3-yne:

A suspension of 7.30g (16.0 mmoles) of 3-phenyl-1,2-propadienyltriphenylphosphonium bromide in 50 ml of anhydrous THF was treated at 0° under nitrogen with 14.8 ml of a 1.15M hexane solution of n-butyllithium. A deep red mixture was obtained and stirred at 25° for 2 hours before being treated with 3.05g (15.0 mmoles) of 2-phenylethynylbenzaldehyde at 25°. The solution was stirred at 25° for 20 hours, poured into 100 ml of water and extracted with 3 X 100 ml of methylene chloride. The organic extracts were combined, washed with 100 ml of water, dried over magnesium sulfate and

concentrated to a brown oil. Thin-layer chromatography (SiO$_2$, 1:2 CH$_2$Cl$_2$-hexane) showed the complete absence of the aldehyde and the appearance of one fluorescent product with a high R$_f$. Column chromatography SiO$_2$) eluting with hexane removed a yellow oil which was treated once with charcoal: yield 3.46g (11.3 mmoles, 75.4%); ir (neat) 2220, 2180 (weak, sharp), 1600, 1490, 1440 (sharp), 955 cm^{-1} (medium).

Attempted Thermal Cyclization of trans-(2'-Phenylethynyl)-1,4-diphenyl-1-en-3-yne:

A mixture of 3.46g (11.4 mmoles) of trans-(2'-phenylethynyl)-1,4-diphenyl-1-en-3-yne in 9.7g of tetralin was deaerated and heated at 175° under nitrogen for 4 hours. The progress of reaction was monitored by hourly thin-layer chromatography. As no apparent changes took place, the mixture was heated at reflux (207°) for 43 hours. Thin-layer chromatography (SiO$_2$, 1:4 CH$_2$Cl$_2$/hexane) indicated no noticeable change.

Column chromatography (SiO$_2$) eluting with hexane separated tetralin and the starting material (identifiable by infrared spectroscopy). Upon standing, the end fraction of tetralin deposited a crystalline material which was isolated by filtration and washing with cold hexane: yield 118 mg (0.388 mmoles, 3.40%); mp 192-193°; ir (KBr) no C=C band at 1600, weak absorptions at 1500, 1370, 890 cm^{-1}; mass spectrum: m/e 304 (M+), no other fragments were observed.

Synthesis of (Z)-2,α'-Dibromostilbene:

A suspension of 3.89g (10.0 mmoles) of benzyltriphenylphosphonium chloride in 100 ml of anhydrous ether was treated at 0° under nitrogen with 15.1 ml of a 0.73-M hexane solution of n-butyllithium (10% excess). The intensely colored ylide was stirred at 25° for 1 hour and then treated with 3.65g (11.0 mmoles) of carbon tetrabromide in 50 ml of anhydrous ether. The mixture was stirred at 25° for 16 hours, cooled to 0° and treated again with 15.1 ml of n-butyllithium. The dark red ylide was stirred at 25° for 1 hour and then allowed to react with 1.67g (8.91 mmoles) of 2-bromobenzaldehyde in 50 ml of anhydrous ether. The resulting mixture was heated at reflux for 2 hours, cooled and mixed with 200 ml of a two-phase CH$_2$Cl$_2$-water

system. The phases were separated and the aqueous phase was extracted with 3X 75 ml CH_2Cl_2. The combined organic extracts were dried over magnesium sulfate and concentrated to a yellow oil which was purified by column chromatography (SiO_2) to give a colorless liquid: yield 2.23g (6.60 mmoles, 74.0%); ir (neat) 1455, 1435 (medium), 1120 (strong), 895 cm^{-1} (medium).

Synthesis of (Z)-2,α'-Di(phenylethynyl)stilbene:

To a deaerated 25-ml triethylamine solution containing 2.23g (6.60 mmoles) of (Z)-2,α'-dibromostilbene and 1.48g (14.5 mmoles) of phenylacetylene, were added 9.7 ng (0.043 mmoles) of palladium[II] acetate and 21.0 mg (0.080 mmoles) of triphenylphosphine. The mixture was heated at 95° for 3.5 hours. After cooling, the white precipitate of triethylamine hydrobromide was removed by filtration: yield 1.93g (indicating 80.3% conversion).

The filtrate was purified by column chromatography (SiO_2) eluting with hexane. The eluate was treated with charcoal and concentrated to yield a yellow solid which was further purified by column chromatography through alumina. The off-white solid obtained showed physical properties consistent with the expected product: yield 515 mg (1.36 mmoles, 20.5%), mp 85-86°; ir (KBr) 1600 (medium), 1495, 1450 cm^{-1} (strong) (Note: This spectrum does not resemble that of 1,4-diphenyl-1,3-butadiyne); mass spectrum: m/e 380 (M+).

Thermal Cis-Trans Isomerization of (Z)-2,α'-Di(phenylethynyl)stilbene (Attempted Thermal Cyclization):

A solution of 514 mg (1.36 mmoles) of (Z)-2,α'-di(phenylethynyl)-stilbene in 1.30g of deaerated tetralin was heated under nitrogen at 175° for 24 hours. The progress of reaction was monitored by thin-layer chromatography at convenient intervals. As tlc did not indicate appreciable change, the mixture was heated at reflux (207°) for 24 hours. Still no appreciable change occurred on tlc. The mixture was purified by column chromatography (SiO_2).

The first hexane eluate contained only tetralin. Subsequent elution superated a yellow solid which was treated with charcoal and recrystallized from petroleum ether: yield 250 mg (29.0%); mp 182-184°; ir (KBr) 1600

(medium), 1495, 1450 (strong), 900 cm^{-1} (strong), mass spectrum: m/e 380 (M+); nmr (CDCl$_3$) δ7.1-8.0 (m, 19H, aromatic) and 8.4 ppm (S, 1H, vinylic).

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